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Calculation of Equilibrium Constants and Activation Energies for Some Reactions Involving Various Isotopic Species of Hydrogen, Water, and Hydrogen Sulfide*

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In part I, by means of statistical-mechanical theory, equilibrium constants are calculated for exchange reactions of the various isotopic forms of hydrogen, water and hydrogen sulfide. The calculations are made over a range of temperature and show the temperature dependence of the reactions. Part II concerns itself with the calculation of activation energies for these various reactions. The computations show that the reactions fall into three main classes. Hydrogen or deuterium, and water or hydrogen sulfide, can be expected to react by a chain mechanism at about 500°C. Water and hydrogen sulfide can be expected to react by either a chain or bimolecular mechanism around 400°C, and the isotopic forms of water or hydrogen sulfide with themselves at 200 to 300°C by a bimolecular mechanism.

INTRODUCTION

ONE of the earliest and most interesting applications of deuterium in chemical research was the preparation of various isotopic molecules and a study of the reactions between them. Knowledge of the equilibria and rates of such reactions is of importance as a preliminary step towards an understanding of more general reactions. Previously many authors[1] have calculated equilibrium constants alone, but these computations are obviously incomplete in the absence of any information concerning the rate of attainment of the equilibrium. In part I of this paper we calculate equilibrium constants from statistical-mechanical theory, and in part II, activation energies have been calculated for many of these same reactions, and conclusions are drawn concerning probable mechanisms.

PART I. EQUILIBRIUM CONSTANTS

Procedure

Two methods for the theoretical calculation of equilibrium constants from a knowledge of molecular constant data have previously been used. One method is indirect and involves calculating ΔE° from spectroscopic data and combining it with a calculated ΔS° to obtain ΔF°, and finally finding K by means of the relation $\Delta F^\circ = -RT \log_e K$.[2]

The statistical-mechanical calculation is much more direct and elegant, and simply depends

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[1] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933); J. Am. Chem. Soc. **56**, 1885 (1934); Crist and Dalin, J. Chem. Phys. **2**, 735 (1934); Farkas and Farkas, Proc. Roy. Soc. (London) **A144**, 467 (1934); T. Förster, Zeits. f. physik. Chemie **B27**, 1 (1934); Farkas and Farkas, Trans. Faraday Soc. 30, 1071 (1934); Urey and Greiff, J. Am. Chem. Soc. **57**, 321 (1935).

[2] See for example, Giauque, J. Am. Chem. Soc. **52**, 4808 (1930); ibid. **52**, 4816 (1930); **54**, 1731 (1932); Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933); Johnston and Long, ibid. **2**, 389 (1934).

upon the fact that an equilibrium constant is expressible as a ratio of the product of the partition functions for the product and reactant molecules.[3] It has been used, for example, by Crist and Dalin and Urey and Greiff[1] and is the method we shall use in this article.

All of the reactions we consider are stoichiometrically bimolecular, with the same number of reactant and product molecules. We may write

$$A+B\rightleftarrows C+D. \tag{1}$$

A, B, C, and D denote di- or triatomic molecules, and in every case C and D are merely different isotopic species of A and B. We have

$$K=F_{(C)}F_{(D)}/F_{(A)}F_{(B)}. \tag{2}$$

Here F denotes the complete partition function for the molecule in question. In practice it is easier to calculate a product of F ratios rather than a ratio of products. Urey and Greiff[1] have given equations for calculating the F ratios for di- and triatomic molecules, but their equations are quite special and only apply to isotopic molecules of the same symmetry number. It is perhaps of interest and importance to arrive at their equations by starting with perfectly general expressions, applicable to all kinds of molecules.

It is assumed that it is a good approximation to express the partition function of a molecule as a product of translational, rotational, and vibrational parts, i.e.,

$$\begin{aligned}F(\text{diatomic molecule})&=F(\text{trans.})F(\text{rot.})F(\text{vibr.})g_m i_m\\&=\frac{(2\pi mkT)^{\frac{1}{2}}V}{h^3}\cdot\frac{8\pi^2 IkT}{\sigma h^2}\cdot\frac{e^{(E_0-\frac{1}{2}hc\omega_0)/kT}}{(1-\exp -hc\omega_0/kT)}g_m\cdot i_m.\end{aligned} \tag{3}$$

The term $((2\pi mkT)^{\frac{1}{2}}V)/h^3$ is the partition function for three degrees of translational motion. V is the volume in which the molecule moves, and the other symbols have their usual meaning.

The expression $(8\pi^2 IkT)/\sigma h^2$ represents the partition function for two degrees of rotational freedom. I is the moment of inertia of the molecule and σ the symmetry number, or number of orientations of the molecule which are physically indistinguishable. σ is 2 for molecules of the type X_2 and 1 for molecules like XY.

The vibrational partition function is $(1-e^{-hc\omega_0/kT})^{-1}$, where ω_0 is the fundamental vibrational frequency of the molecule.

The term $\exp(E_0-\frac{1}{2}hc\omega_0)/kT$ occurs because the zero of energy is taken to be that of the atoms at 0°K rather than that of the molecule. The expression $\frac{1}{2}hc\omega_0$ is the zero-point energy of the system, and E_0 the total energy. $E_0-\frac{1}{2}hc\omega_0$ is the heat of formation of the molecule from its atoms at 0°K.

g_m is a weight factor arising from electron states, and i_m a factor arising from nuclear spins. All the molecules we shall consider are in singlet electronic states, so that $g=1$ and need not be in the expressions explicitly.

From Eq. (3) we have, for diatomic molecules,

$$\begin{aligned}\frac{F_{(C)}}{F_{(A)}}&=\frac{(2\pi m_C kT)^{\frac{1}{2}}V}{h^3}\cdot\frac{8\pi^2 I_C kT}{\sigma_C h^2}\cdot\frac{e^{(E_{0C}-\frac{1}{2}hc\omega_{0C})/kT}}{(1-e^{-hc\omega_{0C}/kT})}i_C\Big/\frac{(2\pi m_A kT)^{\frac{1}{2}}V}{h^3}\cdot\frac{8\pi^2 I_A kT}{\sigma_A h^2}\cdot\frac{e^{(E_0-\frac{1}{2}hc\omega_{0A})/kT}}{(1-e^{-hc\omega_{0A}/kT})}i_A\\&=\left(\frac{m_C}{m_A}\right)^{\frac{3}{2}}\frac{\sigma_A}{\sigma_C}\frac{i_C}{i_A}\frac{I_C}{I_A}\frac{(1-e^{-(hc\omega_{0A}/kT)})}{(1-e^{-(hc\omega_{0C})/kT})}e^{-\Delta E/kT},\end{aligned} \tag{4}$$

where $\Delta E=(E_{0A}-\frac{1}{2}hc\omega_{0A})-(E_{0C}-\frac{1}{2}hc\omega_{0C})$.

For the case of isotopic molecules where $E_{0A}=E_{0C}$, ΔE simply becomes $\frac{1}{2}hc(\omega_{0C}-\omega_{0A})$. If we consider the special case where $\sigma_A=\sigma_C$ and $i_C=i_A$ Eq. (4) reduces to the equation given by Urey and Greiff. (Their paper, Eq. No. (12).) In the case of H_2, HD and D_2 we must use

$$\Delta E'=\left(E_{0A}-\tfrac{1}{2}ch\omega_{0A}+\frac{B_{0A}ch}{4}\right)-\left(E_{0C}-\tfrac{1}{2}hc\omega_{0C}+\frac{B_{0C}hc}{4}\right),$$

[3] See for example, R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1929).

TABLE I. *Molecular constants for diatomic molecules.*

MOLECULE	M (g)	σ	i	I_1/I_2	ω_0	B_e
H_2	2.0162[5]	2	4	$(D_2/H_2)=1.9987$[7]	4371[6]	60.564[6]
HD	3.0228[5]	1	6	$(D_2/HD)=1.499$[7]	3786[6]	45.439[6]
D_2	4.0294[5]	2	9		3092.3[6]	30.312[6]

since the moments of inertia of the molecules are so small. The B_e terms arise from the interaction between rotation and vibration.[4] Eq. (4) then becomes

TABLE III. *F ratios for various isotopic molecules.*

RATIO \ T°K	273.1	298.1	373.1	473.1	573.1	1000
D_2/HD	10.4493	8.9538	6.4893	4.8860	4.0764	2.8487
HD/H_2	33.375	29.397	22.352	17.603	15.114	11.137
D_2/H_2	348.74	263.21	145.05	86.008	61.611	31.726
D_2O/HDO	35.387	26.740	14.555	8.7650	6.3324	3.4323
HDO/H_2O	87.837	69.772	41.868	27.749	20.795	11.798
D_2O/H_2O	3108.2	1865.7	609.39	243.21	131.66	40.497
D_2S/HDS	11.223	9.3075	6.1830	4.4295	3.5867	2.4402
HDS/H_2S	57.150	47.190	31.010	22.050	17.460	11.850
D_2S/H_2S	641.39	439.22	191.73	97.670	62.624	28.916

$$\frac{F_{(C)}}{F_{(A)}}=\left(\frac{m_C}{m_A}\right)^{\frac{3}{2}}\frac{\sigma_A}{\sigma_C}\frac{i_C}{i_A}\frac{I_C}{I_A}\frac{(1-e^{-(hc\omega_{0A})/kT})}{(1-e^{-(hc\omega_{0C})/kT})}e^{-\Delta E'/kT}. \tag{5}$$

The translational partition function for polyatomic molecules is the same as for diatomic molecules. There are, however, now three degrees of rotational freedom, and the rotational partition function becomes $[8\pi^2(8\pi^3ABC)^{\frac{1}{2}}(kT)^{\frac{3}{2}}]/\sigma h^3$, where A, B and C are the three moments of inertia for the molecule in question.

For a polyatomic molecule we therefore have in general,

$$F(\text{polyatomic molecule})=\frac{(2\pi mkT)^{\frac{3}{2}}V}{h^3}\frac{8\pi^2(8\pi^3ABC)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma h^3}\frac{e^{(E_0-\frac{1}{2}\Sigma hc\omega_i)/kT}}{\pi_i(1-e^{-hc\omega_i/kT})}i. \tag{6}$$

TABLE II. *Molecular constants for triatomic molecules.*

MOLECULE	M (g)	σ	i	A_1/A_2[11]	B_1/B_2[11]	C_1/C_2[11]	ω_1	ω_2	ω_3
H_2O	18.0162	2	4	$\frac{(D_2O)}{(H_2O)}=1.798$	1.998	1.929	1595.4[8]	3600[8]	3756.35[8]
HDO	19.0228	1	6	$\frac{(D_2O)}{(HDO)}=1.357$	1.267	1.339	1380[9]	2810[9]	3720[9]
D_2O	20.0294	2	9				1179[9]	2666[9]	2784[9]
H_2S	34.0162	2	4	$\frac{(D_2S)}{(H_2S)}=1.887$	1.998	1.965	1236[10]	2615[10]	2632[10]
HDS	35.0228	1	6	$\frac{(D_2S)}{(HDS)}=1.296$	1.346	1.328	1078[10]	1910[10]	2619[10]
D_2S	36.0294	2	9				898[10]	1906[10]	1940[10]

[4] Mulholland, Proc. Camb. Phil. Soc. **24**, 280 (1928); Sutherland, ibid. **26**, 402 (1930); Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).
[5] F. W. Aston, Nature **137**, 357 (1936).
[6] Jeppeson, Phys. Rev. **44**, 165 (1933).
[7] Calculated.
[8] H. Sponer, *Molekulspektren* (I. Julius Springer, 1935), p. 78.
[9] H. Sponer, ibid., p. 144.
[10] Bailey, Thompson, and Hale, J. Chem. Phys. **4**, 625 (1936).
[11] These ratios have been calculated from formulas derived from definition. For H_2O and D_2O we have, if α is the angle between the O−H or O−D bonds,

$$\frac{B_{(D_2O)}}{B_{(H_2O)}}=\frac{m_{(D)}}{m_{(H)}};\qquad \frac{A_{(D_2O)}}{A_{(H_2O)}}=\frac{m_{(O)}+2m_{(H)}}{m_{(O)}+2m_{(D)}}\frac{B_{(D_2O)}}{B_{(H_2O)}};\qquad \frac{C_{(D_2O)}}{C_{(H_2O)}}=\frac{m_O+2m_D\sin^2\alpha/2}{m_O 2m_H\sin^2\alpha/2}\frac{A_{(D_2O)}}{A_{(H_2O)}};$$

m_H, m_D, and m_O are the masses of the hydrogen, deuterium and oxygen atoms, respectively. For H_2O, $\alpha=104°40'$. For H_2S, $\alpha=111°30'$.

TABLE IV. *Equilibrium constants for isotopic exchange reactions.*

REACTION	CONSTANT	$\Delta\Sigma\omega_i$(cm^{-1})	273.1°K	298.1°K	373.1°K	473.1°K	573.1°K	1000.0°K
(1) $H_2 + D_2 \rightleftarrows 2HD$	$K_1 = \frac{F(HD)}{F(H_2)}\frac{F(HD)}{F(D_2)}$	109	3.19$_4$	3.28$_2$	3.44$_4$	3.60$_3$	3.70$_8$	3.91$_0$
(2) $H_2 + D_2O \rightleftarrows HD + HDO$	$K_2 = \frac{F(HD)}{F(H_2)}\frac{F(HDO)}{F(D_2O)}$	696	0.943$_0$	1.09$_9$	1.53$_6$	2.00$_8$	2.38$_7$	3.24$_5$
(3) $HD + H_2O \rightleftarrows H_2 + HDO$	$K_3 = \frac{F(H_2)}{F(HD)}\frac{F(HDO)}{F(H_2O)}$	−456	2.63$_2$	2.37$_3$	1.87$_3$	1.57$_6$	1.37$_6$	1.05$_9$
(4) $H_2 + D_2S \rightleftarrows HD + HDS$	$K_4 = \frac{F(HD)}{F(H_2)}\frac{F(HDS)}{F(D_2S)}$	278	2.97$_4$	3.15$_8$	3.61$_5$	3.97$_4$	4.21$_4$	4.56$_4$
(5) $HD + H_2S \rightleftarrows H_2 + HDS$	$K_5 = \frac{F(H_2)}{F(HD)}\frac{F(HDS)}{F(H_2S)}$	−291	1.71$_2$	1.60$_5$	1.38$_7$	1.25$_3$	1.15$_5$	1.06$_4$
(6) $D_2 + HDO \rightleftarrows HD + D_2O$	$K_6 = \frac{F(HD)}{F(D_2)}\frac{F(D_2O)}{F(HDO)} = \frac{K_1}{K_2}$	−587	3.38$_7$	2.98$_6$	2.24$_3$	1.79$_4$	1.55$_3$	1.20$_5$
(7) $D_2 + H_2O \rightleftarrows HD + HDO$	$K_7 = \frac{F(HD)}{F(D_2)}\frac{F(HDO)}{F(H_2O)} = K_1K_3$	−347	8.40$_6$	7.79$_2$	6.45$_2$	5.67$_9$	5.10$_1$	4.14$_2$
(8) $HD + D_2S \rightleftarrows D_2 + HDS$	$K_8 = \frac{F(D_2)}{F(HD)}\frac{F(HDS)}{F(D_2S)} = \frac{K_4}{K_1}$	169	0.931$_0$	0.962$_0$	1.05$_0$	1.10$_2$	1.13$_7$	1.16$_7$
(9) $D_2 + H_2S \rightleftarrows HD + HDS$	$K_9 = \frac{F(HD)}{F(D_2)}\frac{F(HDS)}{F(H_2S)} = K_1K_5$	−182	5.46$_9$	5.27$_0$	4.77$_9$	4.51$_3$	4.28$_3$	4.16$_0$
(10) $D_2 + H_2O \rightleftarrows H_2 + D_2O$	$K_{10} = \frac{F(H_2)}{F(D_2)}\frac{F(D_2O)}{F(H_2O)} = \frac{K_1K_3}{K_2}$	−1043	8.91$_3$	7.08$_5$	4.20$_1$	2.82$_6$	2.13$_7$	1.27$_6$
(11) $D_2 + H_2S \rightleftarrows H_2 + D_2S$	$K_{11} = \frac{F(H_2)}{F(D_2)}\frac{F(D_2S)}{F(H_2S)} = \frac{K_1K_5}{K_4}$	−460	1.83$_9$	1.66$_9$	1.32$_2$	1.13$_6$	1.01$_6$	0.911$_4$
(12) $H_2O + D_2S \rightleftarrows D_2O + H_2S$	$K_{12} = \frac{F(D_2O)}{F(H_2O)}\frac{F(H_2S)}{F(D_2S)} = \frac{K_3K_4}{K_2K_5}$	−583	4.84$_6$	4.24$_8$	3.17$_8$	2.49$_0$	2.10$_2$	1.40$_1$
(13) $D_2O + H_2O \rightleftarrows 2HDO$	$K_{13} = \frac{F(HDO)}{F(D_2O)}\frac{F(HDO)}{F(H_2O)} = K_2K_3$	240	2.48$_2$	2.60$_9$	2.87$_7$	3.16$_6$	3.28$_4$	3.43$_5$
(14) $HDO + D_2S \rightleftarrows D_2O + HDS$	$K_{14} = \frac{F(D_2O)}{F(HDO)}\frac{F(HDS)}{F(D_2S)} = \frac{K_4}{K_2}$	−418	3.15$_2$	2.87$_3$	2.35$_4$	1.97$_3$	1.76$_5$	1.40$_7$
(15) $D_2O + H_2S \rightleftarrows HDO + HDS$	$K_{15} = \frac{F(HDO)}{F(D_2O)}\frac{F(HDS)}{F(H_2S)} = K_2K_5$	405	1.61$_5$	1.76$_5$	2.13$_1$	2.51$_6$	2.75$_8$	3.45$_3$
(16) $H_2O + D_2S \rightleftarrows HDO + HDS$	$K_{16} = \frac{F(HDO)}{F(H_2O)}\frac{F(HDS)}{F(D_2S)} = K_3K_4$	−178	7.82$_6$	7.49$_6$	6.77$_1$	6.26$_4$	5.79$_8$	4.83$_5$
(17) $H_2O + HDS \rightleftarrows HDO + H_2S$	$K_{17} = \frac{F(HDO)}{F(H_2O)}\frac{F(H_2S)}{F(HDS)} = \frac{K_3}{K_5}$	−165	1.53$_7$	1.47$_9$	1.35$_0$	1.25$_8$	1.19$_1$	0.995$_7$
(18) $D_2S + H_2S \rightleftarrows 2HDS$	$K_{18} = \frac{F(HDS)}{F(D_2S)}\frac{F(HDS)}{F(H_2S)} = K_4K_5$	−13	5.09$_2$	5.07$_0$	5.01$_5$	4.97$_8$	4.86$_8$	4.85$_6$

Hence, for polyatomic molecules,

$$\frac{F_{(D)}}{F_{(B)}} = \frac{\dfrac{(2\pi m_D kT)^{\frac{3}{2}}V}{h^3}\,\dfrac{8\pi^2(8\pi^3 A_D B_D C_D)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma_D h^3}\,\dfrac{e^{(E_0-\frac{1}{2}hc\Sigma\omega_{0iD}/kT}i_D}{\pi_i(1-e^{-hc\omega_{0iD}/kT})}}{\dfrac{(2\pi m_B kT)^{\frac{3}{2}}V}{h^3}\,\dfrac{8\pi^2(8\pi^3 A_B B_B C_B)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma_B h^3}\,\dfrac{e^{(E_0-\frac{1}{2}hc\Sigma\omega_{0iB})/kT}i_B}{\pi_i(1-e^{-hc\omega_{0iB}/kT})}}$$

$$= \left(\frac{m_D}{m_B}\right)^{\frac{3}{2}}\frac{\sigma_B}{\sigma_D}\frac{i_D}{i_B}\left(\frac{A_D B_D C_D}{A_B B_B C_B}\right)^{\frac{1}{2}}\Pi_i\frac{(1-e^{-hc\omega_{0iB}/kT})}{(1-e^{-hc\omega_{0iD}/kT})}e^{-\Delta E/RT}, \qquad (7)$$

where $\Delta E = (E_{0B} - \frac{1}{2}hc\Sigma\omega_{0iB}) - (E_{0D} - \frac{1}{2}hc\Sigma\omega_{0iD})$.

For isotopic molecules $E_{0B} = E_{0A}$, and therefore $\Delta E = \frac{1}{2}hc(\Sigma\omega_{iD} - \Sigma\omega_{0iB})$. For the cases when $\sigma_B = \sigma_D$ and $i_D = i_B$ Eq. (6) reduces to the zone given by Urey and Greiff. (See their paper Eq. (13).) We now apply Eqs. (5) and (7) to various isotopic molecules. The molecular constants used in the calculations are given in Tables I and II, and the F ratios in Table III.

The values in Table III may be used to calculate equilibrium constants for various reactions, as shown in Table IV.

The equilibrium constants given in Table IV have all been calculated directly from the F ratios shown in Table III. Obviously they are not all independent. The first five, however, may be taken as independent, while the last thirteen may be shown to be expressible in terms of the independent set. Other authors have previously calculated some of the constants of reactions involving isotopic hydrogen and water molecules, but we have repeated these calculations for the sake of the consistency and completeness of Tables III and IV.

The temperature variation of all the equilibrium constants is very largely determined by the exponential term in Eqs. (5) and (7). The value of this exponential term depends upon the differences in zero point energies of the products and reactants. The column in Table IV headed $\Delta\Sigma\omega_i$ gives this difference in cm^{-1}. A study of the table shows clearly that when the zero point energy of the products is greater than that of the reactants (ΔE_0 is positive) the reaction is endothermic and the constant increases with increase in temperature as is to be expected. When the difference in zero point energy is negative, the reaction is exothermic and the constant is found to decrease with increase in temperature. Reaction (18) is interesting in that its change in zero-point energy is practically zero and it is found to be practically independent of temperature.

Crist and Dalin[12] have calculated $1/K_3$ at various temperatures. They used slightly different values for the molecular constants, but their equilibrium constants are in rough agreement with ours. Thus by interpolation we find $1/K_3=0.43$, 0.56, 0.66, 0.74, 0.82, 0.88, and 0.90 at $T=300$, 400, 500, 600, 700, 800, and 900°K, respectively. Crist and Dalin calculated for the corresponding temperatures the values 0.35, 0.51, 0.60, 0.68, 0.74, 0.79, and 0.83. They find experimentally $1/K_3=0.71$ at 799°K.

Farkas and Farkas[13] calculated our $K_1=3.27$ at 293.1°K in perfect agreement with our value. They found experimentally our $K_3=2.67$ at 293.1°K and $K_3=1.15$ at 723°K, while Topley and Eyring[14] calculate $K_{13}=3.26$ at 298.1 and 3.40 at 373.1°K. These values are decidedly higher than ours, and the discrepancy must be sought in a different choice of constants.

The large values for the equilibrium constants at room temperature for reactions (7), (10), (16), and (18) are of interest as well as the large temperature coefficient of reaction (10). Classically the equilibrium constants should approach 1 or 4 as the temperature is increased. It is to be noted that there is considerable departure from the classical values at ordinary temperatures, particularly in the case of reactions (2), (6), (7), (10), (12) and (16).

TABLE V. *Constants used in constructing Morse potential energy curves.*

BOND	$r_0(A°)$	$\omega_0(cm^{-1})$	D(kcal.)
H−H	0.74[16]	4375[16]	102.4[16]
O−H	0.97[16]	3660[16]	113.1[16]
S−H	1.35[8]	2600[8]	87.0[17]
O−O	1.32[18]	1304[19]	34.3[20]
S−S	2.08[18]	510[21]	64.0[20]
S−O	1.7[18]	612[19]	71.0[20]

PART II. ACTIVATION ENERGIES

A knowledge of these constants given in part I is alone incomplete in the absence of any information concerning the rate of the reactions, and we now proceed to calculate the activation

TABLE VI. *Activation energies for reactions between hydrogen, water and hydrogen sulfide.*

REACTION	ACTIVATION ENERGY
(1) $D_2+H_2O \rightleftharpoons HDO+HD$	65.1 kcal.
(2) $D_2+H_2S \rightleftharpoons HDS+HD$	66.4
(3) $D_2O+H_2S \rightleftharpoons HDO+HDS$	49.3
(4) $H_2O+D_2O \rightleftharpoons HDO+HDO$	29.3
(5) $H_2S+D_2S \rightleftharpoons HDS+HDS$	39.4
(6) $D+H_2O \rightleftharpoons HDO+H$	4.9
(7) $D+H_2S \rightleftharpoons HDS+H$	3.5
(8) $D_2+OH \rightleftharpoons HDO+D$	8.7
(9) $D+HDS \rightleftharpoons SH+D_2$	9.7

[12] Crist and Dalin, J. Chem. Phys. **2**, 548 (1934).
[13] Farkas and Farkas, Trans. Faraday Soc. **30**, 1071 (1934).
[14] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).
[15] For references see Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935).
[16] R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932).
[17] Calculated from data in Bichowski and Rossini's *Thermochemistry*.
[18] Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).
[19] Calculated.
[20] Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).
[21] D. Clark, Chem. Rev. **11**, 231 (1932).

energies in order to draw some conclusions about the rates.

Calculations

The method of calculating activation energies is the so-called semiempirical system of Eyring which has been described elsewhere.[15] We simply give in Table V the constants used for constructing the various Morse curves.

Results

The reactions, with their calculated activation energies are given in Table VI.

All of the reactions given in Table IV, except number 1[22] are merely isotopic variations of reactions (1) to (5) in Table VI, and their activation energies will differ only slightly from the values given for the above reactions due to small differences in zero point energies.

For each of the above reactions (1) to (5) we must now consider, in addition to a bimolecular mechanism, a chain mechanism.

Reaction (1): $D_2+H_2O\rightleftarrows HDO+HD$

If the mechanism of this reaction is bimolecular the activation energy is as given in Table VI. However, the following chain mechanism appears plausible:

$$D_2\rightleftarrows 2D, \quad (1)$$
$$D+H_2O\rightleftarrows HDO+H, \quad (2)$$
$$H+D_2\rightleftarrows HD+D. \quad (3)$$

By the usual methods[23] it may be shown that for this mechanism the over-all activation energy for reaction (1) is equal to the activation energy of reaction (2), plus one-half the heat of dissociation of D_2, or $A=52.3+4.9=57.2$ kcal. Reaction (1) is the thermal dissociation of deuterium.

Reaction (2): $D_2+H_2S\rightleftarrows HDS+HD$

If this reaction is kinetically bimolecular the activation energy is as given in Table VI. The following chain mechanism is also possible:

$$H_2S\rightleftarrows H+HS, \quad (1)$$
$$H+D_2\rightleftarrows HD+D, \quad (2)$$
$$D+H_2S\rightleftarrows HDS+H. \quad (3)$$

For this mechanism $A=\frac{1}{2}D_{S-H}+A_2=43.5+9.1=52.6$ kcal. D_{S-H} signifies the heat of dissociation of the S−H bond. The thermal dissociation of H_2S rather than D_2 is considered because the S−H bond is weaker than the D−D bond.

Reaction (3): $D_2O+H_2S\rightleftarrows HDO+HDS$

The activation energy for the bimolecular mechanism of this reaction is given in Table VI. The following chain mechanism must also be considered.

$$H_2S\rightleftarrows H+HS, \quad (1)$$
$$H+D_2O\rightleftarrows HDO+D, \quad (2)$$
$$D+H_2S\rightleftarrows HDS+H. \quad (3)$$

Here $A=\frac{1}{2}D_{S-H}+A_2=43.5+6.3=49.8$ kcal.

Reaction (4): $H_2O+D_2O\rightleftarrows HDO+HDO$

The activation energy for this reaction, if it is kinetically bimolecular, is given in Table VI. The following chain mechanism, however, also suggests itself.

$$H_2O\rightleftarrows H+OH, \quad (1)$$
$$H+D_2O\rightleftarrows HDO+D, \quad (2)$$
$$D+H_2O\rightleftarrows HDO+H. \quad (3)$$

Here $A=\frac{1}{2}D_{O-H}+A_2=56.6+6.3=62.9$ kcal.

Reaction (5): $H_2S+D_2S\rightleftarrows HDS+HDS$

The activation energy for this reaction, if it has a bimolecular mechanism, is given in Table VI. However, the following chain mechanism is also possible.

$$H_2S\rightleftarrows H+HS, \quad (1)$$
$$H+D_2S\rightleftarrows HDS+D, \quad (2)$$
$$D+H_2S\rightleftarrows HDS+H. \quad (3)$$

$A=\frac{1}{2}D_{S-H}+A_2=43.5+4.4=47.9$ kcal.

The preceding results are summarized in Table VII.

Discussion

The energies given in Table VII lead to some interesting conclusions. Thus, we see that the reactions between D_2 and H_2O, or D_2 and H_2S, both involve high activation energies, and both would be expected to go via a chain mechanism in the vicinity of 500°C because in forming the activated complex in the bimolecular mechanism

[22] Reaction (1) of Table IV is not included in Table VI because it has been thoroughly studied previously. See Hirschfelder, Eyring, and Topley, J. Chem. Phys. **4**, 170 (1936), and L. Farkas and E. Wigner, Trans. Faraday Soc. **32**, 708 (1936).

[23] Cf. Sherman, Quimby and Sutherland, J. Chem. Phys. **4**, 732 (1936).

TABLE VII. *Activation energies for molecular and chain mechanisms.*

REACTION	ACTIVATION ENERGY (kcal.)	
	Bimolecular Mechanism	Chain Mechanism
(1) $D_2 + H_2O \rightleftarrows HDO + HD$	65.1	57.2
(2) $D_2 + H_2S \rightleftarrows HDS + HD$	66.4	52.6
(3) $D_2O + H_2S \rightleftarrows HDO + HDS$	49.3	49.8
(4) $H_2O + D_2O \rightleftarrows HDO + HDO$	29.3	62.9
(5) $H_2S + D_2S \rightleftarrows HDS + HDS$	39.4	47.9

the hydrogen atoms are very close together, hence the repulsions are very large, necessitating a high energy requirement for its formation.

The reaction between D_2O and H_2S would be expected to proceed at a somewhat lower temperature, around 450°C, and as far as the calculations can show, both the bimolecular mechanism and the chain mechanism are about equally probable.

The exchange reactions between light and heavy water or light and heavy hydrogen sulfide should occur around 200 to 300°C and the bimolecular mechanism leads to a much lower activation energy than the chain mechanism proposed.

In view of the comparative scarcity of kinetically bimolecular reactions now known, reactions (4) and (5) are especially interesting. It is of interest to point out qualitatively the factors which lead to low activation energy for a bimolecular reaction. In both reactions (4) and (5) the H and D atoms are small compared to the O and S atoms. This means that in the activated complex, the H and D atoms are comparatively far apart, and hence the repulsion between them is small. Also, the O−O and S−S bonds are rather weak, so that the repulsions between these atoms are also rather small. These small repulsions lead to a comparatively stable activated complex, and hence a low activation energy.

It must be remembered that the above conclusions are really valid only under rather special conditions. The calculations apply to the reactions when they are carried out in the gas phase in the absence of catalysts such as walls, oxygen, moisture, light, impurities, etc. Also, the conclusions concerning mechanisms apply only when the reaction is far removed from equilibrium—i.e., at the beginning of the reaction. Moreover, the particular radical mechanisms suggested, although the most plausible, are not necessarily unique. For example, in reaction (5), it might be possible to postulate a free radical mechanism which leads to an activation energy lower than 39.4 kcal., although no such mechanism yet suggests itself.

There are several experimental studies of exchange reactions between deuterium and water, and between light and heavy water, but these have all been carried out catalytically.[24]

Conclusions

Equilibrium constants for various isotopic exchange reactions between hydrogen, water and hydrogen sulfide have been calculated. In the gas phase and in the absence of catalysts the various types of reactions considered fall into three classes:

1. The exchange reactions between isotopic species of hydrogen and water, and hydrogen and hydrogen sulfide will occur at high temperatures (500°C) and via chain mechanisms.

2. The exchange reactions between isotopic species of water and hydrogen sulfide will occur around 400°C and via a bimolecular and chain mechanism.

3. The exchange reactions between various isotopic species of water, and of hydrogen sulfide will occur around 200 to 300°C and via a bimolecular mechanism.

We wish to express our appreciation to Professors Norris F. Hall and Farrington Daniels for their constant interest in this paper. This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

[24] Bonhoeffer and Rummel, Naturwiss. **22**, 45 (1934); L. Farkas and A. Farkas, Trans. Faraday Soc. **30**, 107 (1934); A. Farkas and L. Farkas, J. Chem. Phys. **2**, 468 (1934); A. Farkas, Trans. Faraday Soc. **32**, 922 (1936).

A Thermal Conductivity Method for the Determination of Isotopic Exchanges in the Simpler Gaseous Molecules

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(Received February 15, 1937)

A simple high pressure thermal conductivity gauge of good mechanical stability, freedom from poisoning effects and high accuracy has been described in detail. Its physical characteristics have been studied and optimum conditions for operation indicated. Its applicability to a wide variety of analyses is discussed and specific data quoted for those of the isotopic isomers of the lower aliphatic hydrocarbons and the hydrogens. Methods of direct calibration for the latter substances are indicated as well as a technique for their separation and purification. The theory of the gauge is developed and compared with experimental observations on the hydrogen isotopes.

SINCE the discovery of the heavy hydrogen isotope, deuterium, and its use by the physical chemist as an aid in elucidating the kinetics of reactions several workers in the field have developed thermal conductivity gauges for the purpose of isotopic analysis. In general they were operated with mixtures of the hydrogens, advantage being taken of the large specific heat differences which exist between the isotopic molecules H_2, HD and D_2 at low temperatures—such as those in the liquid-air region. Both high and low gas pressures have been employed. An adequate review of the early work in this field is to be found in A. Farkas' book *Light and Heavy Hydrogen*. Subsequent to the work included above, Sachsse and Bratzler[1] developed a thermal gauge, for use on the hydrogen isotopes, which operated at high pressures (~200 mm) and room temperatures, thus making direct use of the differences in thermal conductance due alone to the mass differences involved. They claimed high precision for their gauge. Still more recently Reitz and Bonhoeffer[2] have published results obtained with a Pirani manometer whereby the analysis is carried out directly upon samples of isotopic water vapor.

Our experiences with several of the abovementioned types of gauges[3] showed quite definitely that they possessed characteristics which made them difficult to operate. Recently Wirtz[4] published a paper indicating some of these difficulties attendant upon the Farkas low pressure gauge. The accommodation coefficient plays a dominant role in such low pressure gauges and, as is well known to workers in this field, is a very temperamental factor placing serious limitations on the attainable accuracy. With these difficulties in mind we attempted to develop a simple thermal gauge—operating at higher pressures so as to eliminate accommodation coefficient effects—of rugged construction and yet of sufficiently high reproducibility and precision that it could be used to analyze directly the amounts of isotopic exchanges in the simpler compound gaseous molecules.

It is felt that the results to be presented in this paper adequately show that all these characteristics have been attained. Our gauge has been used with completely satisfactory results in a series of recent researches involving exchange reactions,[5, 6] and has proved itself a practical tool. Because of the difficulties which seem to be encountered in the construction and operation of this type of analytical device it was deemed advisable to describe our gauge in detail. For these reasons it is felt that its publication may prove of value to other workers in the field.

THE APPARATUS

The gauge itself, Fig. 1, consists of a fine bare platinum wire *A* (0.0008 inch diam.) mounted coaxially in a $\frac{1}{8}$-inch hole bored through the center of a $\frac{1}{2}$-inch rolled brass rod *B*. The

[1] Sachsse and Bratzler, Zeits. f. physik. Chemie **171A**, 332 (1934).
[2] Reitz and Bonhoeffer, Zeits. f. physik. Chemie **174A**, 427 (1935).
[3] Mr. E. A. Smith and others, private communication.
[4] K. Wirtz, Zeits. f. physik. Chemie **32B**, 334 (1936).
[5] Trenner, Morikawa and Taylor, J. Chem. Phys. 5, 203 (1937).
[6] Morikawa, Trenner and Taylor, J. Am. Chem. Soc. in press.

brass rod is 6 inches long and the platinum wire $4\frac{7}{8}$ inches long. The wire *A* is held concentric by means of the recessed Bakelite bushing *C* through the centers of which it passes, tiny holes being provided for that purpose. These holes are of a size just sufficient to permit the two heavy platinum leads (No. 28 B & S gauge) *D* to pass through them. The lower lead-in *D* passes out through the brass bushing *E* and the whole is soldered into the bottom of the brass rod *B*. The upper bushing *C* is bored with a second hole by means of a No. 50 drill and is located off center. This hole permits free entry and exit of the gases introduced into the gauge. Above the upper lead-in wire is a tungsten spring *F* (~diameter 5–7 mils) which serves to keep the wire *A* taut. Finally this spring is connected to a heavy tungsten (60 mil) lead sealed through the ground-in Pyrex head *G*. This head was carefully ground into the 3° taper machined on to the end of the brass tube *B* and waxed into it—during final assembly—by means of a thin film of de Khotinsky cement. The fitted joint was covered in turn with a film of gum sandarac to prevent penetration of the thermostat oil. The gases were led into the gauge by means of the 1–2 mm Pyrex capillary tube *H* which was fused to the head *G*. Heavy copper wires (No. 18 B & S gauge) connected to the tungsten lead-in on the head and the platinum lead at the bottom served to make electrical connections to the gauge. All internal connections in the gauge were carefully brazed.

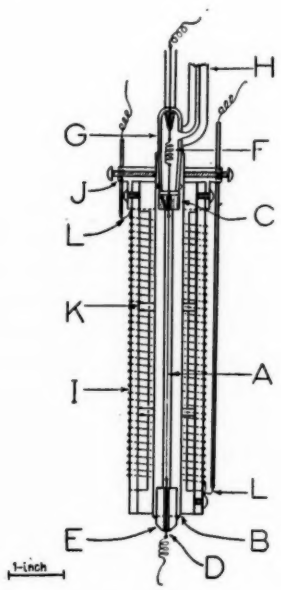

FIG. 1.

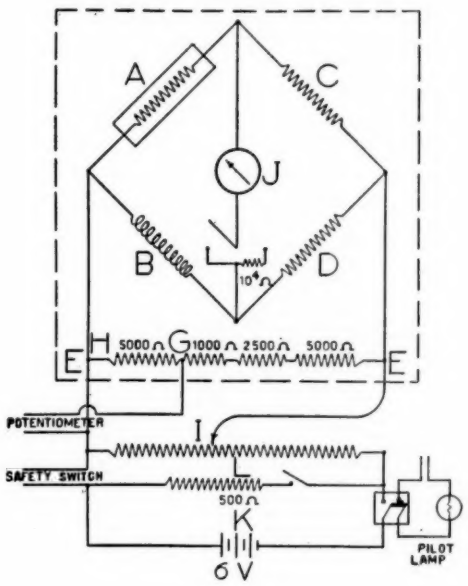

FIG. 2.

Concentrically about the gauge tube *B* was rigidly fastened a fiber or Catalin[7] frame I. This frame is of $\frac{3}{4}$-inch internal diameter, 6 inches long and is threaded symmetrically over 5 inches of its surface with a 28 standard thread. Six $5 \times \frac{3}{8}$-inch slots were cut into it longitudinally to allow free passage of the oil through it to the gauge within. The whole frame was supported by means of a flanged brass collar *J* and its three set screws, as well as by the two thin brass spacers *K* ($\frac{1}{8}$ inch thick and soldered to the gauge tube *B*) machined so that the frame just slipped over them. On the threaded portion of this frame were *tightly* wound about 30 feet of (No. 36 B & S gauge) pure platinum wire the ends of which were securely fastened by means of tiny set screws and to which were soldered two heavier copper wires *L* (No. 28 B & S gauge) for electrical connections. The whole was carefully insulated from the gauge tube *B* and its connecting wires. As will be evident later, the

[7] Blank tubes of Catalin may be obtained from the American Catalin Corporation, New York. Fiber is not especially recommended for this purpose because of poor machining qualities and a tendency to shrink when submerged in oil.

compensator winding should be made of as heavy a gauge platinum wire as practical to compact winding. In no case should it be made of much lighter gauge than that suggested above inasmuch as it is essential to proper operation of the gauge that this winding remain at the thermostat temperature and suffer as little heating due to the current flow as possible. This condition is more closely attained by exposing the wires of the winding as much as possible to free flow of oil around them, hence the grid-like form of the supporting frame.

The electrical circuit used is given in Fig. 2, the dynamic portion enclosed within the dotted lines being immersed beneath the thermostat oil (kerosene). This oil was carefully dried and purified by treatment with activated charcoal. All connections were heavily soldered and the entire dynamic part of the circuit, by being immersed beneath the thermostat oil, was held quite constant in characteristics while at the same time annoying variations due to parasitic currents were eliminated. *A* indicates the gauge, *B* the compensator, *C* and *D* two bare manganin (No. 22 B & S gauge) wound balancing resistors fully exposed to the thermostat oil but mounted on a Bakelite panel and finally the voltage dividing resistors *E* and *E*. These latter were made of a suitable combination of No. 231 type Shallcross *wire wound* 10 watt resistors mounted rigidly on a Bakelite frame. At points *G* and *H* was connected a good potentiometer—such as the Leeds and Northrup type K—capable of reading up to 1.6 volts and accurate to five decimal places. A 2-volt storage cell of high capacity—such as the Willard type DH-5-1—was used to feed the potentiometer. *I* is a special voltage divider made by winding a length of bare manganin wire (No. 24 B & S gauge) equivalent to ~100 ohms (~110 feet) on a grooved (11 turns per inch) Catalin drum, $4\frac{1}{2}$ inches in diameter and 10 inches long, which was mounted on two heavy brass bearings so that the drum could be rotated smoothly. In order to insure good contact through these bearings the axles were allowed to project somewhat and laminated phosphor-bronze brushes installed between the bearing plates and the axle ends. The threaded or grooved section of the drum surface was 8 inches long. A small traveling wheel with a fine V groove on its outer edge was mounted on a long brass axle. This served as the moving contact represented by the arrow on *I* in Fig. 2. The wheel axle was mounted on a heavy spring-brass support which served to keep the wheel pressed firmly against the wire on the drum. Rotation of the drum caused the contact wheel to travel along the drum wire. Occasional cleaning and light greasing with a dilute solution of vaseline in petroleum ether always resulted in positive contact between wire and contact wheel, an important detail in this work. The entire mechanism was mounted on a heavy Bakelite base $\frac{1}{2}$-inch thick. The entire instrument was mounted inside a wooden case with a tight fitting removable cover. This protected the winding from dust and laboratory fumes which attack manganin wire. All moving contacts were avoided where possible and all connections heavily soldered. Where bearings could not be avoided they were made massive to insure low positive contact resistance. The manganin wire on the rotating drum had its ends soldered to the bearing plates at the drum ends. A fine vernier for rotating the drum at final adjustment proved of value. A scale was mounted along the contact wheel axle and another on the drum end so as to allow the contact wheel to be put at the approximate position before closing the main switch. This proved a great convenience in rapidly setting the voltage to the approximate value required and also served to protect the galvanometers, which nevertheless had high resistances put in their circuits for protection against unduly large currents. These latter were removed at final adjustment. The galvanometer *J* was a high sensitivity (12 microvolts per mm) *low* internal resistance (>25 ohms) instrument. It was operated critically damped. Finally the whole circuit was fed from a high capacity six-volt storage cell *K*. It is important that this cell deliver a *steady voltage* under moderate current drain. In order to obtain a constant voltage from the storage cells it was found good practice to shunt them with a moderately high resistance *L* (~500 to 1000 ohms) when not in use during periods of analysis and for about one hour before measurements are begun. This bleeding process helps to maintain a very constant voltage during an entire days operation and certainly removed

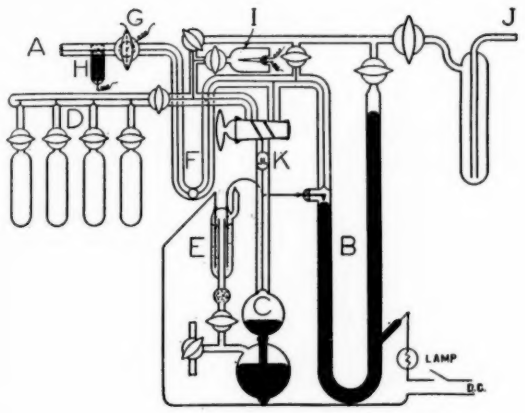

FIG. 3.

the initial drift on starting measurements, which proved very annoying. All the various parts in the Wheatstone bridge circuit should be very securely mounted within the thermostat bath. The suggestions given regarding the compensator design and construction especially should be followed.

The thermostat bath consisted of a tank about 12 in.×12 in.×14 in. equipped with a good stirrer located directly beneath the gauge so that the oil stream passed rapidly about the latter. When used in conjunction with a vacuum tube relay of the type described by Heisig and Gernes[8] no difficulty was found in holding the bath temperature to better than 0.001°, provided the stirring was sufficiently *rapid* and *constant*. The bath temperature was adjusted so as to be about 3° above average laboratory conditions—26.35°C in our case—and heating was provided by means of a 40-watt electric light bulb completely immersed in the oil.

The thermostat used should be one which operates with the smallest possible heating and cooling cycles since their magnitude to a large degree determines the attainable precision of the gauge. The absolute temperature is of very much less importance as will be seen later from temperature coefficient data. The reason for this appears to be twofold. First, because of the practical impossibility of obtaining platinum wires for both the gauge and compensator of the same temperature coefficients of resistivity—in our case they differed by 7 percent—and second because of the inevitable thermal lag between gauge tube and compensator. The entire set-up was entirely free from susceptibility to vigorous vibration or shock. This condition is not difficult to attain and is essential for successful operation.

The auxiliary apparatus for manipulation of the gases is shown in Fig. 3. In order that measurements could be carried out on as small an amount of gas sample as possible the dead space was kept as small as possible. To this end, all connections between the gauge *A* and its manometer *B* were made with 1–2 mm capillary tubing. The volume of gas necessary for our gauge was 4.3 cc S.T.P. The operation of the remainder of the apparatus is obvious. *C* is a small Toepler pump of ~100 cc capacity used to transfer the gas from the sampling tubes—attached to manifold *D*—to the gauge as well as for adjusting the gas pressure within the gauge. This adjustment was accurately and automatically attained by means of the electrolyzer *E*. The latter operated on a small current through the contacts sealed into the manometer at the desired positions. On turning on the current the electrolytic gas would slowly drive the mercury piston up until contact was broken at the desired pressure—about 200–230 mm. This method was highly satisfactory and gave reproducible results although our gauge readings were not excessively sensitive to pressure, as will be seen later from the pressure coefficient data of our gauge. The remainder of the apparatus consisted of a good high vacuum pumping system with a two-stage mercury vapor pump connected at *J*. The trap *F* served to exclude mercury and water vapors as well as other impurities from the gauge. Various refrigerants were used about it depending on the nature of the gas under investigation. *K* is a tiny grease trap.

Since it was found that *violent* overheating of the gauge wire resulted in serious disturbance of the thermal conductivity measurements and even in possible burn-out, it was considered good practice to introduce a safety switch mounted directly on the plug of stopcock *G*. This prevented pumping out the gauge with the gauge current on and thus possible serious overheating of the gauge wire due to evacuation

[8] Heisig and Germes, Ind. and Eng. Chem., Anal. Ed. **6**, 155 (1934).

of the gas from the gauge. The device consisted of a bent platinum wire, mounted to the back of the stopcock plug, which dipped into a pool of mercury H only when the stopcock was closed. Electrical connection was established by means of a phosphor bronze or silver "pig tail." It was placed directly in the main battery line and proved entirely satisfactory, always giving positive contact. The small tube I of about 20 cc capacity contained a small platinum filament which could be brought to a dull red glow by electrical heating. This served to equilibrate the hydrogen isotopes where that condition did not already exist in the gas samples. This, as we shall see later, was essential to correct analysis of the hydrogen isotopes. To measure the vacuum attained during pumping out, the thermal gauge was itself used as a vacuum gauge after calibration against a McLeod gauge. A pressure of $\sim 10^{-6}$ mm Hg was always required before analysis of a gas was undertaken. For this purpose a tapping key, shunted across the safety switch G, served to allow the gauge to be actuated during vacuum measurement. In assembling the gauge it was found good practice to glow the fine platinum wire in air for a short time, by means of a small gas flame, just before slipping it into place in the brass tube B. This process appears to remove all traces of oxidizable material from the wire surface and anneals away any strains introduced during drawing. It was found to introduce excellent stability characteristics to the wire. All the gauge parts were scrupulously cleaned of oil and grease before assembly.

Adjustment of the Gauge Circuit

To adjust the bridge circuit quickly, the following procedure was observed. Following assembly of the gauge, its internal resistance was measured at the thermostat temperature using a current so small that heating of the wire was negligible—this was found to be ~ 65 ohms for our gauge. Next, its internal resistance at a temperature $\sim 20°$ higher was measured using a similar small current—this was found to be ~ 69.5 ohms for our gauge. The length of the compensator wire was now adjusted so that its total resistance at the thermostat temperature about equaled that of the gauge at the same temperature. Finally the two manganin resistors C and D were wound and their respective resistances matched to those of the compensator and gauge—at the higher temperature—respectively, and placed in the appropriate arms of the bridge circuit. When this circuit was now brought to balance the gauge wire was heated to about 20° over the bath temperature, independent of the nature of the gas present around it. The voltage dividing resistors E–E were so selected that the tap-off to the potentiometer had about one-third of the total potential drop over the bridge, across it. Our combination consisted of 5000 ohms between points F and H and 8500 ohms between points H and M.

Theory of the Gauge

It is a well-known result of kinetic theory that the thermal conductivity of a gas for the condition that the mean free path of its molecules is small compared to the distance between the boundaries defining the temperature gradient is given by the Maxwell-Chapman-Enskog equation:

$$\lambda = \Lambda \frac{Cv}{M^{\frac{1}{2}}\sigma^2}, \tag{1}$$

where Λ is a constant of the particular system used, Cv the specific heat at constant volume, M the molecular weight and σ the molecular diameter. For a gas mixture of i species of molecules and assuming the thermal conductivities of each species to be independent of the presence of the other, Eq. (1) becomes:

$$\lambda = \sum_i \frac{Cv_i C_i}{M_i^{\frac{1}{2}}\sigma_i^2}, \tag{2}$$

where C_i is the mole fraction of the ith kind of molecule. The relative thermal conductivity of such a gas mixture to some standard reference gas 1 becomes then:

$$\frac{\lambda'}{\lambda} = \sum_i \left(\frac{Cv_i C_i}{M_i^{\frac{1}{2}}\sigma_i^2} \Big/ \frac{Cv_1}{M_1^{\frac{1}{2}}\sigma_1^2} \right). \tag{3}$$

If I' and I_1 are the respective currents through the gauge wire to establish a given temperature

gradient in the gauge when the gases i and 1 are present and if r is the resistance of the wire under these conditions then since $\lambda = i^2 r\Delta$ it follows that Eq. (3) becomes

$$\frac{(I')^2}{I_1^2} = \left(\sum_i \frac{Cv_i C_i}{M_1^{\frac{1}{2}}\sigma_i^2} \Big/ \frac{Cv_1}{M_1^{\frac{1}{2}}\sigma_1^2}\right) = \frac{(E')^2}{E^2} = (R')^2. \quad (4)$$

E' and E_1 are the respective voltages across the whole Wheatstone diamond necessary to produce balance with the respective gases and obviously $I \propto E$. For the special case of the thermal conductivities of isotopic molecules Eq. (4) can be further simplified since it has been found[9] that their molecular diameters are identical. It has been assumed that this condition holds for all cases of isotopic molecules. From Eq. (4) we see that the ratio $R' = E'/E_1$ should be independent of the condition of the wire, the bath temperature —provided that C_v is independent of the temperature—and independent of the total pressure used—again provided that C_v is independent of the pressure. Actually the value of R' is found only to approximate these conditions due, in part, to failure to meet the above provisions and due to the presence of unknown amounts of heating in the compensator winding and convection currents in the gauge itself. Thus, for precise results, the gauge must be calibrated with samples of known concentrations.

The Hydrogens

In the case of the hydrogen isotopes certain special conditions obtain which permit Eq. (4) to be amplified. If we define a quantity $p = \mathrm{D}/\mathrm{H}+\mathrm{D}$, where D equals the number of atoms of deuterium per unit volume and H is the corresponding quantity for protium then p is the atom fraction of D in the gas, and if, further, we assume that the equilibrium $H_2 + D_2 \rightleftarrows 2HD$ has been established at temperatures sufficiently high that the equilibrium constant $K = 4$ then it easily follows that the relations,

$$\begin{aligned} C_{H_2} &= (1-p)^2, \\ C_{HD} &= 2p - 2p^2, \\ C_{D_2} &= p^2, \end{aligned} \quad (5)$$

are satisfied. C is the mole fraction.

In addition, at 300°K, the values of C_{vD_2} and C_{vHD} are identical and equal to 4.989 while C_{vH_2} is 4.908 so that Eq. (4) becomes

$$R_p^2 = \frac{E_p^2}{E_{H_2}^2} = \frac{\frac{0.983}{M_{H_2}^{\frac{1}{2}}}(1-p)^2 + \frac{(2p-2p^2)}{M_{HD}^{\frac{1}{2}}} + \frac{p^2}{M_{D_2}^{\frac{1}{2}}}}{0.983/M_{H_2}^{\frac{1}{2}}}, \quad (6)$$

a form very similar to that arrived at by Sachsse and Bratzler[2] for their gauge. For mixtures of H_2 and D_2 this equation would become

$$R^2 = \frac{E_p^2}{E_{H_2}^2} = \frac{\frac{0.983}{M_{H_2}^{\frac{1}{2}}}(1-p) + \frac{p}{M_{D_2}^{\frac{1}{2}}}}{0.983/M_{H_2}^{\frac{1}{2}}}. \quad (7)$$

Operation of the Gauge

After setting up the gauge and its auxiliary apparatus the whole system was thoroughly outgassed for twenty-four hours and the vacuum followed from time to time, liquid air being used on the trap F. When constant over a period of time the system was ready for measurement. A few cubic centimeters of carefully purified hydrogen were withdrawn from a storage bulb by means of the Toepler and *slowly* introduced into the gauge through the liquid-air trap until the manometer cuts off. The gauge stopcock was then closed and the drum voltage divider I rotated until balance was obtained. Readings on the potentiometer were now taken until constancy was obtained, usually within one minute after the current was turned on. In general the first determination after the gauge has been standing was not very reliable and consequently served only as an orientation result. When not in use the best practice was found to be to leave the gauge under vacuum. In working with other gases it was found best to use the pure light isotopic compound as the standard substance for checking the condition of the wire. Thus, in the case of heavy hydrogen analysis, light hydrogen was used as the standard substance while, for

[9] Van Cleave and Maass have shown by viscosity and thermal conductivity measurements that σ_{D_2} and σ_{H_2} cannot be very different and so we considered

$$\sigma_{H_2} = \sigma_{HD} = \sigma_{D_2}.$$

Van Cleave and Maass, Can. J. Research **12**, 57 (1935); ibid. **12**, 372 (1935).

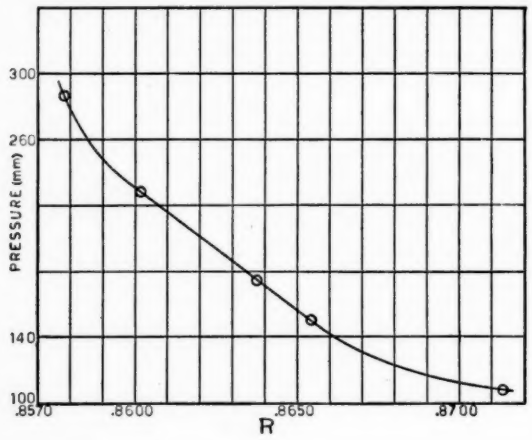

FIG. 4.

analysis of the methanes, CH_4 was the standard substance. Such procedure was found to yield the highest precision. Of course, only gases of the highest purity should be used. The hydrogens used were prepared by electrolysis from caustic soda solutions using platinum electrodes in an all glass system, traces of oxygen being removed by slow passage over a long glowing platinum filament and water by slow passage through a glass wool packed liquid-air trap.

CHARACTERISTICS OF THE GAUGE

The gauge was found to possess excellent stability during operation and seemed quite free from poisoning effects. Exposure to air or oxygen was found to be without any deleterious influence on the wire and reproducible values of R could be obtained immediately after exposure to them. Even accidental mild overheating of the wire or complete replacement of the wire by a new one left R essentially unchanged although the absolute values of E_{H_2} and E_{D_2} were markedly changed. This proved a very desirable property, for although the values of E_{H_2} and E_{D_2} were subject to slow drifts—over several days time—the values of R proved quite reproducible. In anticipation one might point out that these characteristics were found to hold for all the gases studied, including CH_4, C_2H_6 and C_3H_8. Thus for one platinum wire the value of R between a given pair of samples of H_2 and D_2 was found to be 0.85962. After overheating the wire this value was found to be 0.86014. On replacing the wire by a new one a value of 0.85948 was found for R. During a series of measurements with H_2 over a period of eight hours the absolute value of E_{H_2} was found to vary by less than 0.1 of a millivolt.

The pressure and temperature dependences of the gauge are given in Fig. 4 and Table I, respectively. It will be noted that over the small range of temperatures studied the value of R is a good constant as anticipated by theory. However, R has a pressure dependence due in part to the differential heating effect in the compensator and in part to changes in the convective losses. This dependence is not large, however, and introduces no operational difficulties. It may be further reduced by a heavier compensator winding. It will be noted that the gauge was operated on the linear range of the curve in Fig. 4. In this range the pressure dependence of R was -6.8 units of spread per millimeter. Since the composition dependence of R was about -14.3 units of spread per percent deuterium one sees that to obtain an accuracy of 0.1 percent the pressure must be adjusted to 0.21 mm. This is easily attained with the method used.

CALIBRATION OF THE GAUGE

In order to calibrate the gauge for the hydrogen isotopes, equilibrated samples of known atom percent of deuterium were prepared by electrolysis of 17 cc of a 2 percent solution of caustic soda in about 50 percent D_2O using platinum electrodes. As the water electrolyzed away, samples ($\sim$200 cc) of the hydrogen gas were taken from time to time and analyzed for their D content by means of a quartz fiber gas density balance to be described elsewhere.[10] These values were accurate to ± 0.1 percent. The unequilibrated samples were made synthetically by mixing known

TABLE I. *The temperature dependence. Pressure of gas = 229 mm Hg.*

THERMOSTAT TEMPERATURE °C	E_{D_2} (volts)	E_{H_2} (volts)	R
24.00	1.28900	1.50115	0.85868
25.00	1.29389	1.50712	0.85852
26.00	1.29872	1.51302	0.85846
26.32	1.30007	1.51425	0.85856

[10] Trenner, J. Am. Chem. Soc. forthcoming paper.

amounts of pure H_2 and D_2 of ~99 percent purity.[11] The R values of these mixtures were determined directly and again after bringing them to equilibrium in the platinum wire equilibrator. These latter R values served to determine their precise D atom concentration from the calibration curve for equilibrated gases previously determined. These data are graphed in Fig. 5.

It will be noted that the change in the thermal conductivity on equilibration of the mechanical mixtures is small. This is due to the fact that, since the specific heats of all the molecular species involved are practically identical under our conditions, the only difference arises from the failure of the proportion $\sqrt{2} : \sqrt{3} = \sqrt{3} : \sqrt{4}$ to be true of the mass terms. Thus the production of 2HD from H_2 and D_2 results in a gas of slightly higher conductivity. Despite the smallness of the change in R which occurs on equilibration—even of a 50 percent mixture of D_2 and H_2—an accuracy of 2–3 percent is attainable which, for some kinetic studies, would be adequate. Thus rates of approach to equilibrium of the hydrogen isotopes could be studied using this gauge.

In order to fit Eq. (6) to the observed data of the equilibrated gases it was found necessary to introduce three coefficients—α_{H_2}, α_{HD} and α_{D_2}—before each of the terms, respectively. A partial justification for this arises from the value of R obtained for pure D_2 (by short extrapolation of the calibration curve). The best value was found to be 0.8568 which when put into the equation

$$\alpha_{D_2}=\frac{\alpha_{H_2}R_{D_2}{}^2C_{v_{H_2}}M_{D_2}{}^{\frac{1}{2}}}{C_{v_{D_2}}M_{H_2}{}^{\frac{1}{2}}}$$

along with the appropriate values of the other terms and $\alpha_{H_2}=1$, gives $\alpha_{D_2}=1.022$. This correction coefficient arises from a small differential heating effect in the compensator winding as well as from the inevitable presence of differential convection losses. The former error can be minimized by heavier winding on the compensator, the latter by the use of baffles in the conductivity tube, and by horizontal instead of vertical mounting of the whole gauge. Using this value of α_{D_2} and $\alpha_{H_2}=1$ we now fit the equation:

[11] The author wishes to express his indebtedness to Mr. E. A. Smith of this laboratory for the preparation of these samples.

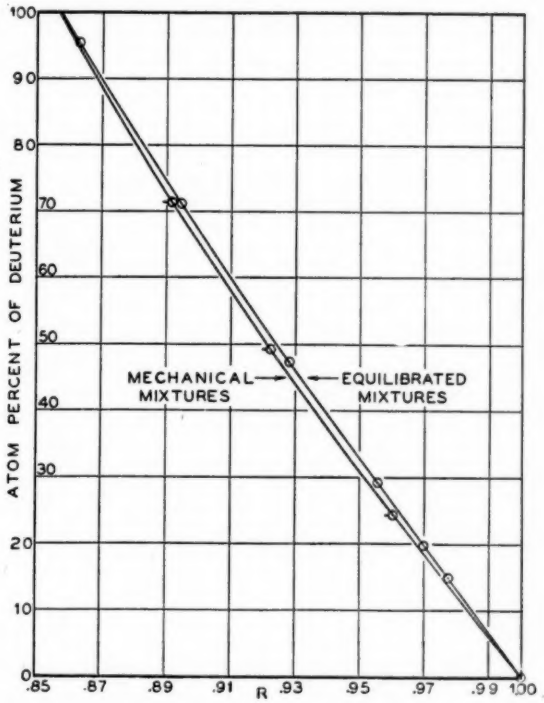

FIG. 5. Calibration curve for the hydrogen isotopes. Temperature = 26.35°C. Pressure = 229 mm Hg.

$$R_p{}^2=[\alpha_{H_2}(0.983/M_{H_2}{}^{\frac{1}{2}})(1-p)^2+\alpha_{HD}((2p-2p^2)/M_{HD}{}^{\frac{1}{2}})+\alpha_{D_2}(p^2/M_{D_2}{}^{\frac{1}{2}})]/[0.983/M_{H_2}{}^{\frac{1}{2}}] \quad (8)$$

to the observed data by arbitrarily selecting the value of α_{HD} and using $C_{v_{D_2}}=4.987$, $C_{v_{H_2}}=4.908$, $C_{v_{HD}}=4.988$, $M_{H_2}=2.016$, $M_{HD}=3.022$, $M_{D_2}=4.029$. A value of $\alpha_{HD}=1.013$ was found to give the best fit. This fit is illustrated by the data given in Table II. On putting the numerical values in Eq. (8) it becomes on transposition:

$$p=\frac{0.5500-0.3025-0.6351(1-R^2)}{0.1837}. \quad (9)$$

The maximum deviation between Eq. (9) and the observed data is 0.5 percent at the lower values of p and 0.2 percent at the higher values. Such agreement is sufficient for most work and since the gauge described is easy to reproduce—being entirely machined in its important parts—it should be possible to use Eq. (9) in those cases in which direct calibration is not possible, although the method of known synthetic mixtures is certainly more desirable and precise. In consideration of the results of direct calibration and

general reproducibility we consider our relative results accurate to somewhat better than 0.1 percent and the absolute values to ±0.1 percent. Not more than ten minutes is required for a determination. If results of the highest possible precision are desired the unknown determination should be sandwiched between determinations on the standard substance so as to eliminate small errors due to the small drift of the wire characteristics. This is not necessary for average work, however.

Analysis of the Isotopic Aliphatic Hydrocarbons. The Methanes

Methane presented by far the most difficult purification problem. This is due to two causes. Firstly the spread of the thermal conductivities of CH_4 and CD_4 is not large due to an overlapping of the mass and specific heat effects thus making desirable, measurements of the highest precision and, in consequence, gas samples of the highest purity. Secondly the high vapor pressure displayed by CH_4 and CD_4 at normal liquid-air temperatures made its fractionation from traces of the fixed gases such as O_2, N_2, H_2, etc. rather difficult. Experience showed that the most reliable procedure to employ for the purification of the methanes was to use a special low temperature trap and to distill the sample into it at low pressures ~1 mm with continuous pumping and then subsequently to collect the purified sample by raising the trap temperature to normal liquid-air temperatures and Toeplering off into a sampling bulb. The details of this trap and the method of obtaining the necessary low temperatures have been described elsewhere.[5] The method of preparation of the methanes used has also been fully described in another place.[12] The methods employed for preparing the methane samples obtained from a reaction system prior to analysis of their C−D content is fully described elsewhere.[13]

Table II.

R_p[2] (Observed)	$p\times10^2$ (Observed)	$p\times10^2$ (Calculated)
0.7349	100	100
0.7446	95.5	95.4
0.7999	71.4	71.2
0.8614	47.3	46.9
0.9131	29.2	28.7
0.9402	19.7	19.2
0.9553	14.8	14.2
1.0000	0	0

The results given for the thermal conductivity of CH_4 were obtained by investigation of several samples and by successive purifications until check results were obtained. A similar procedure was employed with CD_4 except that, in addition, exhaustive deuterizations were first carried out on a nickel catalyst. After the final deuterization both the CD_4 and the hydrogens in equilibrium with it were analyzed. From a knowledge of the equilibrium constant

$$K=\frac{C-D}{C-H}\times\frac{H}{D}$$

previously determined by infrared analysis and found to be 1.8[12] and the value of H/D of the hydrogens, the value of C−D/C−H for the best CD_4 was estimated. This was found to be 98.0 percent C−D in good agreement with previous estimates made by infrared analysis.[14] To obtain a calibration point on the curve, a known mixture of the two standardized samples of CH_4 and CD_4 was made up and its conductivity determined. Although this mixture was not brought to equilibrium, we feel that no great error was introduced—as would have occurred had this method been used with the hydrogen isotopes—because of the very small mass difference. The error introduced is certainly within the experimental error. In this way the calibration data for Fig. 6 were obtained.

The operation of the gauge was carried out in a manner entirely analogous to that employed for the hydrogens except that a solid carbon dioxide-acetone bath was substituted for liquid air around the gauge trap *F*. A carefully purified sample of CH_4 was used as the standard reference substance. Valuable gas samples could always be returned to their bulbs after analysis, by means of the Toepler pump, with very little loss and if condensible in liquid air with no loss at all. (Such procedure was always used when pure deutero-

[12] Morikawa, Benedict and Taylor, J. Am. Chem. Soc. **58**, 1445 (1936).

[13] Morikawa and Trenner, Ind. Eng. Chem., Anal. Ed. forthcoming paper.

[14] Benedict, Morikawa, Barnes and Taylor, J. Chem. Phys. **5**, 1 (1937).

hydrocarbons were being worked with.) It will be observed that the curve is *not* linear as would be expected from Eq. (4) for this case. Furthermore the slope is positive pointing to the fact that the specific heat of CD_4 is greater than that of CH_4 and so completely overcomes the effect on the thermal conductance to be expected from the mass ratio alone. These effects were found to be true of all the isotopic isomers of the aliphatic hydrocarbons studied. The accuracy of analysis is only about 1 percent due to the relatively small spread.

The Ethanes

The problem of the ethanes proved a much simpler one, inasmuch as purification was relatively easy and a method for direct preparation of an ethane of known intermediate composition was worked out. For the methods of purification used, reference should be made to the paper previously indicated.[13] For the preparation of the standard intermediate ethane[15] complete details are given in another publication[16] and so will not be repeated here except to indicate that controlled deuterization of ethylene on a copper catalyst at low temperatures was the reaction employed. The purest C_2D_6 of known composition was obtained in an entirely analogous manner to that employed for obtaining CD_4. The results of our calibration are shown in Fig. 6. An equilibrium constant

$$K=\frac{\text{C}-\text{D}}{\text{C}-\text{H}}\times\frac{\text{H}}{\text{D}}=2.4$$

was used, estimated from results previously obtained.[17] It will be noticed that they follow in general form those obtained from the methanes. The gauge operation was identical with that for the methanes. Due to the greater specific heat difference between C_2H_6 and C_2D_6 obtaining in this case over that for the methanes a larger spread results and a consequent *greater* analytical accuracy of at least 0.5 percent accrues.

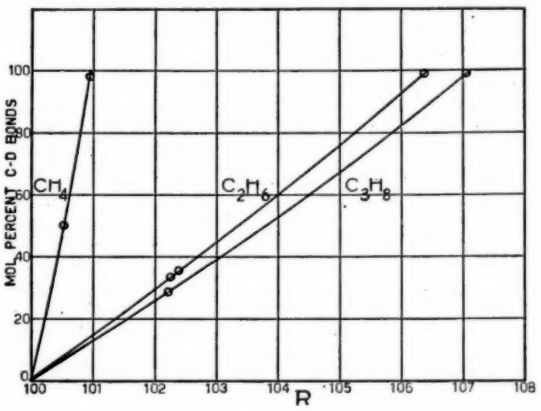

FIG. 6. Calibration curves for the isotopic isomers of the aliphatic hydrocarbons. Temperature = 26.35°C. Pressure = 229 mm Hg.

The Propanes

This substance presented an entirely analogous problem to that of ethane and thus the method of treatment was entirely parallel. The method of preparing the partially deuterized propane of known composition is fully described elsewhere[16] as are the methods of purification.[13] In operation of the gauge the only change made was the use of a −50° bath on trap *F*. The calibration results shown in Fig. 6 again parallel those obtained for the methanes and ethanes except that the specific heat difference is larger than either of the former as would be expected. The analytical accuracy increases apace and is better than 0.5 percent. The value of the equilibrium constant

$$K=\frac{\text{C}-\text{D}}{\text{C}-\text{H}}\times\frac{\text{H}}{\text{D}}$$

used was 2.34.[16]

Analyses on Other Gases

At the present time only rough measurements have been made on the butanes and so no reliable data can be presented. However, these preliminary experiments indicate that no difficulties are encountered using a technique similar to that used on the lower hydrocarbons. The trap bath *F* must be raised to −25° for this work. Longer pumping periods are required due to the solubility of the butanes in the stopcock grease.

The ammonias have been investigated, and in this case it was found that the mass and specific heat effects almost cancel each other with the

[15] Intermediate propanes can also be made in an analogous way.
[16] Morikawa, Trenner and Taylor, J. Am. Chem. Soc. 5, 203 (1937).
[17] Morikawa, Benedict and Taylor, J. Am. Chem. Soc. 58, 1795 (1936).

result that the analytical spread is too small to permit sufficient accuracy to be attained. Obviously combinations of the gases studied in this research can be analyzed for by the thermal conductivity method described and several such analyses have been made by the author.[13] It is planned to use this method of analysis in general on the isotopic isomers of neon, oxygen and carbon. Simple calculation shows that $C^{13}H_4$ and $C^{12}H_4$ could be determined with an accuracy of about 0.5 percent since in this case no marked specific heat differences appear possible. The important features which the compound to be used for thermal analysis must have are relatively small "dead" mass and either very large or negligible specific heat differences for the isotopic isomers.

That this type of thermal conductivity gauge has proved a powerful tool in the investigation of a wide variety of researches concerned with the kinetics of general aliphatic hydrocarbons is amply indicated by several of the papers referred to above. Its most notable feature is its easy adaptation to carrying out analyses on *both* the hydrogens and the hydrocarbons permitting therefore a very complete study to be made of both the kinetics and the equilibria in any hydrogen isotope–lower aliphatic hydrocarbon system, provided only a correct separational procedure is adopted.

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On the Fundamental Frequencies of CH_2, CHD, CD_2, CHCl, CDCl, and *Cis* and *Trans* $C_2H_2D_2$ and $C_2H_2Cl_2$

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A valence force treatment of the groups CH_2, CHD, CD_2, CHCl, CDCl is given. The relative dependence of the three fundamental frequencies calculated for each group on the deformation force constant is used as a guide in correlating these frequencies with the three individual modes of vibration of the group. On the basis of this calculation, an assignment of the fundamental frequencies of *cis*, *trans* and asymmetric $C_2H_2D_2$ calculated by Manneback and Verleysen is given. Also from the data on the degrees of depolarization of the Raman lines of *cis* $C_2H_2Cl_2$ and *trans* $C_2H_2Cl_2$, intensity and selection rules in Raman effect and infrared absorption, an assignment of the fundamental frequencies of these isomers is suggested.

I. INTRODUCTION

THE molecules C_2H_4, C_2D_4, C_2Cl_4 belong to the symmetry type V_h, the *cis* $C_2H_2D_2$ or $C_2H_2Cl_2$ to the type C_{2v}, and the *trans* $C_2H_2D_2$ or $C_2H_2Cl_2$ to the type C_{2h}. Each molecule possesses twelve fundamental vibrations, nine of which take place in the plane of the molecule, and two in directions perpendicular to the plane. One is the torsional vibration. The symmetrical properties and the selection rules in the infrared and the Raman effect can be summarized in Table I.[1]

In C_2H_4, except for the torsional vibration which is inactive in both the infrared and the Raman effect, there is little doubt concerning the other eleven frequencies. These frequencies are given in Table II. For the vibrations S_1 and A_1, Sutherland and Dennison[2] obtained a potential function with four constants. For the nine vibrations in the plane of the molecule, Bonner[3] obtained a potential function containing eight constants, while Manneback and Verleysen[2] determined one with eleven constants. With this potential function and on the assumption that it is invariant under a substitution by an isotope, Manneback and Verleysen calculated the nine frequencies of the vibrations in the molecular plane of each of the *cis*, *trans* and asymmetric $C_2H_2D_2$. The determinantal equation in each case separates into two; one of the 5th degree for the five π', S, π vibrations in the case of the *cis*, *trans* and asymmetric $C_2H_2D_2$, respectively, and one

[1] See, for example, Placzek, *Leipziger Vorträge* (1931).

[2] G. Sutherland and D. M. Dennison, Proc. Roy. Soc. **A148**, 250 (1935).

[3] Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

TABLE I. *Fundamental vibrations of C_2H_4, cis, trans and asymmetric $C_2H_2X_2$. The notation of the symmetry character is that of Manneback and Verleysen.*[4]

	C_2H_4			*cis* $C_2H_2X_2$			*trans* $C_2H_2X_2$			asym. $C_2H_2X_2$		
NOTATION	Sym.	Infra.	Raman	Sym.	Infra.	Raman	Sym.	Infra.	Raman	Sym.	Infra.	Raman
$\nu_{\pi s}$	S_1	—	*s.p.*	π'	*M*	*s.p.*	*S*	—	*s.p.*	π	*L*	*p.*
$\nu_{\pi a}$	A_1	*L*	—	σ'	*L*	*d.*	*A*	—	—	π	*L*	*p.*
$\delta_{\pi s}$	S_1	—	*s.p.*	π'	*M*	*s.p.*	*S*	—	*s.p.*	π	*L*	*p.*
$\delta_{\pi a}$	A_1	*L*	—	σ'	*L*	*d.*	*A*	—	—	π	*L*	*p.*
$\nu_{2\pi s}$	S_1	—	*s.p.*	π'	*M*	*s.p.*	*S*	—	*s.p.*	π	*L*	*p.*
$\nu_{\sigma s}$	S_2	—	*w.d.*	σ'	*L*	*d.*	*S*	—	*s.p.*	σ	*M*	*d.*
$\nu_{\sigma a}$	A_2	*M*	—	π'	*M*	*s.p.*	*A*	—	—	σ	*M*	*d.*
$\delta_{\sigma' s}$	S_2	—	*w.d.*	σ'	*L*	*d.*	*S*	—	*s.p.*	σ	*M*	*d.*
$\delta_{\sigma' a}$	A_2	*M*	—	π'	*M*	*s.p.*	*A*	—	—	σ	*M*	*d.*
$\delta_{\sigma' s}$		—	*w.d.*		—	*d.*	*S'*	—	*d.*		*G*	*d.*
$\delta_{\sigma' a}$		*G*	—		*G*	*d.*	*A'*		—		*G*	*d.*
Torsion		—	—		—	*d.*	*A'*		—		—	*d.*

π, σ =sym. or antisym. with respect to the C=C axis,
π', σ' =sym. or antisym. with respect to an axis perpendicular to the C=C axis in the plane of the molecule,
S, *A* =sym. or antisym. with respect to the center of symmetry,
$S_1=(\pi\pi')$, $S_2=(\sigma\sigma')$, $A_1=(\pi\sigma')$, $A_2=(\pi'\sigma)$.
For the Raman effect, *s* =strong, *w* =weak, *p* =polarized ($\rho<\frac{3}{4}$), *d* =depolarized ($\rho=\frac{3}{4}$).
For the infrared, *L*, *M*, *G* signify change of electric moment along axis of least, middle, and greatest moment of inertia, respectively.
A dash signifies inactive frequency.

of the 4th degree for the corresponding four σ', A, σ vibrations. There is no question as to the accuracy of these calculated frequencies; but the way in which these frequencies are obtained and tabulated does not make it clear which frequency should be assigned to a particular one of the vibrations of the same symmetry group. This can be done in general only by considering the transformation equations between the generalized coordinates used and the normal coordinates. We attempt, however, in this note to give a very plausible assignment by considering the fundamental frequencies of the groups CH_2, CHD, CD_2 from which the three isomers of $C_2H_2D_2$ are formed.

There has been considerable work on the Raman spectra of these isomers.[5] The degrees of depolarization of the Raman lines have been studied by Heidenreich,[6] Paulsen[7] and Trumpy.[8] The Raman spectra of the two isomers of $C_2D_2Cl_2$ have also been studied by Trumpy.[8] The infrared absorption spectra of these isomers have been investigated by Wu[9] in the region between 2 and 23μ. A classification of the Raman frequencies has been given by Trumpy. But from considerations of the vibrations of CHCl, it seems to need modification. It seems possible to give also a reasonable assignment of the infrared frequencies, although the present data are still not sufficient for a definite assignment of some of the fundamental frequencies of these isomers.

II. FUNDAMENTAL VIBRATIONS OF CH_2, CHD, CD_2

The fundamental frequencies of these groups can be treated either by a valence force system or by a noncentral force system. We shall give here a valence force treatment, as the noncentral force treatment leads to similar results.

The valence force treatment of the motion of a three-particle system has been given by Lechner.[10]

TABLE II. *Assignment of fundamental frequencies of cis, trans and asym. $C_2H_2D_2$ calculated by Manneback and Verleysen.*

NOTATION	C_2H_4	*cis* $C_2H_2D_2$	*trans* $C_2H_2D_2$	asym. $C_2H_2D_2$	C_2D_4
$\nu_{\pi s}$	3019.0	π' 2304	*S* 2291	π 3004	2283.9
$\nu_{\pi a}$	2988.0	σ' 2229	*A* 2233	π 2221	2152.5
$\delta_{\pi s}$	1343.9	π' 1248	*S* 1240	π 1043	1008.9
$\delta_{\pi a}$	1444.0	σ' 1295	*A* 1308	π 1357.8	1072.8
$\nu_{2\pi s}$	1621.3	π' 1516.5	*S* 1514.2	π 1555	1428.8
$\nu_{\sigma s}$	3069	σ' 3031	*S* 3049	σ 3088	2308.0
$\nu_{\sigma a}$	3170	π' 3065	*A* 3053	σ 2316	2325.0
$\delta_{\sigma s}$	950	σ' 820	*S* 808	σ 945.6	758.3
$\delta_{\sigma a}$	949.7	π' 752.7	*A* 765.3	σ 725	678.1

[4] C. Manneback and A. Verleysen, Nature **138**, 367 (1936).
[5] Kohlrausch, *Smekal-Raman Effekt.*
[6] Heidenreich, Zeits. f. Physik **97**, 277 (1935).
[7] Paulsen, Zeits. f. physik. Chemie **B28**, 123 (1935).
[8] B. Trumpy, Zeits. f. Physik **98**, 672 (1935).
[9] T. Y. Wu, Phys. Rev. **46**, 465 (1934).
[10] F. Lechner, Graz Dissertation; Monatsh. f. Chem. **61**, 385 (1932).

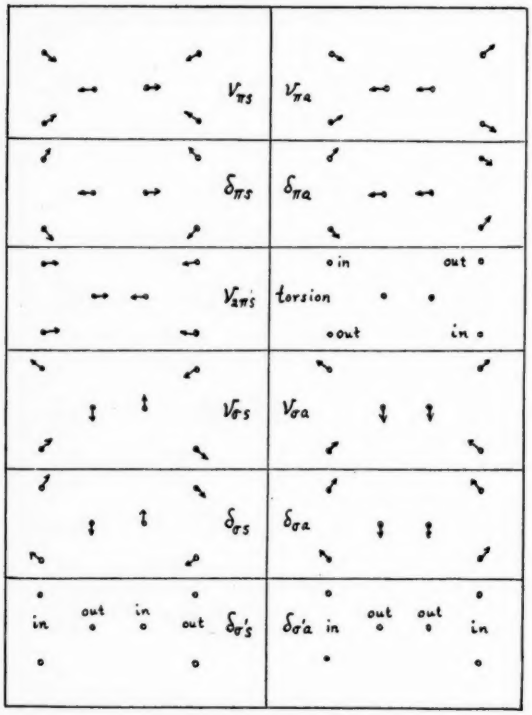

FIG. 1. Modes of vibrations of $C_2H_2X_2$ type molecules.

Let the potential energy of the system be

$$2V=K_1(\Delta r_{12})^2+K_2(\Delta r_{23})^2+\delta(s\Delta\alpha)^2$$

where S is a length. The fundamental frequencies are then given by the three equations

$$\begin{aligned}&\nu_1^2+\nu_2^2+\nu_3^2=K_1/\mu_1+K_2/\mu_2+\delta/\mu_4,\\ &\nu_1^2\nu_2^2+\nu_2^2\nu_3^2+\nu_3^2\nu_1^2\\ &\quad=K_1K_2/\mu_1\mu_2\cdot(1-\mu_1\mu_2\cos^2\alpha/m_2^2)\\ &\quad\quad+(K_1/\mu_1+K_2/\mu_2)\delta/\mu_4\\ &\quad-(K_1/r_{23}^2+K_2/r_{22}^2)\delta s^2\sin^2\alpha/m_2^2,\\ &\nu_1^2\nu_2^2\nu_3^2=K_1K_2\delta/\mu_1\mu_2\mu_4\cdot(1-\mu_1\mu_2/m_2^2),\end{aligned}\qquad(1)$$

where $1/\mu_1=1/m_1+1/m_2$, $1/\mu_2=1/m_3+1/m_2$, $1/\mu_4=s^2(1/\mu_1r_{12}^2+1/\mu_2r_{23}^2-2\cos\alpha/m_2r_{12}r_{23})$. For symmetric molecules, $K_1=K_2$, $m_1=m_3$, $m_2=M$, $r_{12}=r_{23}=s$, the Eqs. (1) become[11]

$$\begin{aligned}&\nu_3^2=K_1(1/\mu-\cos\alpha/M),\\ &\nu_3^2(M+2m)K_\alpha=m^2M\nu_1^2\nu_2^2(1/\mu-\cos\alpha/M),\\ &\nu_1^2+\nu_2^2=K_1(1/\mu+\cos\alpha/M)\\ &\quad\quad+K_\alpha(1/\mu-\cos\alpha/M)/s^2,\end{aligned}\qquad(2)$$

where $K_\alpha=2\delta s^2$, $1/\mu=1/m+1/M$.

For CH_2, the constants K_1 and K_α can be determined from the values of its three fundamental frequencies.[12] In C_2H_4, the vibrations $\nu_{\pi a}$, $\delta_{\pi a}$ correspond to the vibrations ν_1, ν_2, respectively, of the two groups of CH_2 (see Fig. 3). In the approximation of Sutherland and Dennison,[3] $\nu_{\pi a}$ and $\delta_{\pi a}$ are independent of the force constant of the two carbon atoms. Hence the frequencies $\nu_{\pi a}$, $\delta_{\pi a}$ of C_2H_4 are essentially equal to ν_1 and ν_2, respectively, of CH_2. The vibration $\nu_{\sigma a}$ of C_2H_4 consists of two CH_2 groups vibrating in ν_3 with no relative displacement of the carbon atoms. Hence we may take $\nu_3=\nu_{\sigma a}(C_2H_4)$. Thus $\nu_3\cong3100$, $\nu_2\cong1440$, $\nu_1\cong2988$. On substituting $m_1=m_3=1$, $M=12$, $\alpha=115°$, $r_{12}=r_{23}=s=1.08\times10^{-8}$, Eqs. (2) give

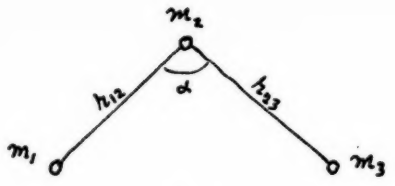

FIG. 2.

$$\begin{aligned}&K_1=5.0\times10^5\text{ dynes/cm},\\ &K_\alpha=1.28\times10^{-11}\text{ dyne cm/radian}.\end{aligned}\qquad(3)$$

For CD_2, with the use of K_1 and K_α for CH_2 (Eqs. (3)), Eqs. (2) give

$$\nu_1=2164,\quad\nu_2=1065,\quad\nu_3=2292,$$

which are comparable with the values A_1 2152.5, A_1 1072.8 and A_2 2325 of C_2D_4 obtained by Manneback and Verleysen.

For CHD, $K_1=K_2$, $r_{12}=r_{23}=s$, $m_1=1$, $m_3=2$, $m_2=12$, $\alpha=115°$, Eqs. (1) give

$$\begin{aligned}&\nu_1^2+\nu_2^2+\nu_3^2=5/3\cdot K_1+1.575K_\alpha/2s^2,\\ &\nu_1^2\nu_2^2+\nu_2^2\nu_3^2+\nu_3^2\nu_1^2\\ &\quad=0.630K_1^2+2.614K_1K_\alpha/2s^2,\\ &\nu_1^2\nu_2^2\nu_3^2=0.985K_1^2K_\alpha/2s^2,\end{aligned}\qquad(4)$$

where the ν's are expressed in units of 1000 cm^{-1} and the K_1, $K_\alpha/2s^2$ in units of 0.5875×10^{-5} dynes/cm. Using the values of K_1, K_α in (3), we have

$$\begin{aligned}&\nu_1^2+\nu_2^2+\nu_3^2=15.65,\\ &\nu_1^2\nu_2^2+\nu_2^2\nu_3^2+\nu_3^2\nu_1^2=66.50,\\ &\nu_1^2\nu_2^2\nu_3^2=66.60.\end{aligned}\qquad(4')$$

[11] W. Penney and G. Sutherland, Proc. Roy. Soc. **A156**, 654 (1936).

[12] These are taken by Sutherland and Dennison from OCH_2 to be $\nu_1=2970$, $\nu_2=1444$, $\nu_3=3000$. We prefer, however, to obtain them from C_2H_4, although the difference in the values of the force constants determined from the two sets of values of $\nu_1\nu_2\nu_3$ is small and would not affect greatly our result below.

Solution of (4′) gives

$$\nu_1=2240\ \text{cm}^{-1},\quad \nu_2=1204\ \text{cm}^{-1},\quad \nu_3=3034\ \text{cm}^{-1}$$

approximately. To show that 2240, 1204 and 3034 correspond, respectively, to the modes of vibration ν_1, ν_2, ν_3, let us consider the dependence of ν_1, ν_2, ν_3 on the deformation constant K_α or $\delta=K_\alpha/2s^2$. For symmetric molecules, it is seen from Eqs. (2) that ν_3 is independent of K_α, while ν_1 and ν_2 depend on K_α. For CHD, the motions are no longer symmetric, but one would still expect ν_3 to depend on K_α not so strongly as ν_1 and ν_2. Writing Eqs. (4) in the form

$$\begin{gathered}\nu_i^2+\nu_j^2+\nu_k^2=5/3\cdot K_1+\alpha\delta,\\ \nu_i^2\nu_j^2+\nu_j^2\nu_k^2+\nu_k^2\nu_i^2=0.630K_1^2+\beta\delta,\\ \nu_i^2\nu_j^2\nu_k^2=\gamma\delta,\end{gathered}$$

where $\alpha=1.575$, $\beta=22.2$, $\gamma=71.3$, one readily obtains

$$\begin{aligned}d\nu_i/d\delta&=-\nu_i[\nu_i^2\alpha+\nu_j^2\nu_k^2/\delta-\beta]\\&\qquad/2(\nu_i^2-\nu_j^2)(\nu_k^2-\nu_i^2),\\ d\nu_j/d\delta&=-\nu_j[\nu_j^2\alpha+\nu_k^2\nu_i^2/\delta-\beta]\\&\qquad/2(\nu_j^2-\nu_k^2)(\nu_i^2-\nu_j^2),\\ d\nu_k/d\delta&=-\nu_k[\nu_k^2\alpha+\nu_i^2\nu_j^2/\delta-\beta]\\&\qquad/2(\nu_k^2-\nu_i^2)(\nu_j^2-\nu_k^2).\end{aligned}\qquad(5)$$

Expressing ν's in units of 1000 cm^{-1}, δ in units of 0.5875×10^5 dynes/cm, we have

$\nu_i=2.240$, $d\nu_i/d\delta=0.011$, or 19 $\text{cm}^{-1}/10^5$ dynes/cm.

$\nu_j=1.204$, $d\nu_j/d\delta=0.054$, or 92 $\text{cm}^{-1}/10^5$ dynes/cm.

$\nu_k=3.100$, $d\nu_k/d\delta<0.00145$, or <2.5 $\text{cm}^{-1}/10^5$ dynes/cm.

The strong dependence of the frequency 1204 cm^{-1} on the deformation force constant and the exceedingly slight dependence of 3034 cm^{-1} on it leave no doubt as to the correctness of the assignment $\nu_1=2240$ cm^{-1}, $\nu_2=1204$ cm^{-1}, $\nu_3=3100$ cm^{-1}.

III*a*. *Cis* $C_2H_2D_2$

From Table I, it is seen that the five π' vibrations correspond to the S_1 and A_2 vibrations of C_2H_4, and the four σ' vibrations correspond to the A_1 and S_2 vibrations of C_2H_4. There is little doubt that the frequency 1516.5 corresponds to $\nu_{2\pi s}$ of C_2H_4. In the following we shall for convenience denote a vibration by the notation of the corresponding vibration of C_2H_4. The vibrations $\delta_{\pi s}$, $\delta_{\pi a}$ are essentially the deformation vibration ν_2 of CHD, and should not be greatly different from each other. From the calculation above, $\nu_2=1204$. Hence the π' 1247.9 and the σ' 1295.4 must be the frequencies $\delta_{\pi s}$ and $\delta_{\pi a}$. The vibrations $\delta_{\sigma s}$ and $\delta_{\sigma a}$ in C_2H_4 consist essentially in a relative vibration of the two CH_2 groups and have low frequencies. It is apparent that in *cis* $C_2H_2D_2$, $\delta_{\sigma s}=\sigma'$ 820.2, $\delta_{\sigma a}=\pi'$ 750.7. Of the vibrations $\nu_{\pi s}\nu_{\pi a}$, $\nu_{\sigma s}\nu_{\sigma a}$, one expects for mechanical reasons that $\nu_{\pi s}$ and $\nu_{\pi a}$ would not be greatly different from each other, nor would $\nu_{\sigma s}$ and $\nu_{\sigma a}$. Since $\nu_{\sigma s}$, $\nu_{\sigma a}$ are essentially the ν_3 vibration of CHD, and $\nu_{\pi s}$, $\nu_{\pi a}$ the ν_1 vibration of CHD, it is seen from our calculation of CHD that $\nu_{\pi s}=\pi'$ 2304.2, $\nu_{\pi a}=\sigma'$ 2228.9, $\nu_{\sigma s}=\sigma'$ 3031, $\nu_{\sigma a}=\pi'$ 3065. This assignment is given in Table II.

III*b*. *Trans* $C_2H_2D_2$

In this molecule, the five S vibrations correspond to the S_1S_2 vibrations, and the four A vibrations to the A_1, A_2 vibrations of C_2H_4. Similar argument as given above for *cis* $C_2H_2D_2$ leads to the assignment in Table II.

III*c*. Asymmetric $C_2H_2D_2$

In this case the five π frequencies correspond to the S_1, A_1 vibrations, and the four σ frequencies correspond to the S_2, A_2 vibrations of C_2H_4. That the assignment $\delta_{\pi s}=\pi$ 1043.1, $\delta_{\pi a}=\pi$ 1357.8, $\nu_{2\pi s}=\pi$ 1555.3, $\delta_{\sigma s}=\sigma$ 945.6, $\delta_{\sigma a}=\sigma$ 724.8 is reasonable is evident from the general trend of the corresponding frequencies in C_2H_4, *cis* and *trans* $C_2H_2D_2$ and C_2D_4. But as the two frequencies π 3004.3 and σ 3088.1 are of different symmetry character and so are π 2221.0 and σ 2316.3, one must now make the assignment

$$\left.\begin{matrix}\nu_{\pi s}\\ \nu_{\pi a}\end{matrix}\right\}=\left\{\begin{matrix}\pi\ 3004.3\\ \pi\ 2221.0,\end{matrix}\right.\qquad\left.\begin{matrix}\nu_{\sigma s}\\ \nu_{\sigma a}\end{matrix}\right\}=\left\{\begin{matrix}\sigma\ 3088.1\\ \sigma\ 2316.3,\end{matrix}\right.$$

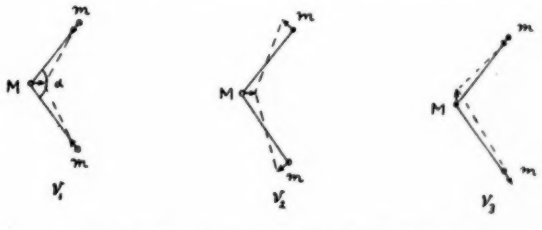

FIG. 3. Fundamental vibrations of CH_2.

and in this case it seems that one cannot distinguish between the two alternative assignments without studying the transformation relations between the generalized coordinates and the normal coordinates.

IV. Fundamental Vibrations of CHCl, CDCl

We may treat the vibrations of CHCl and CDCl by the valence force method as the interaction between the Cl and the H or D atom is smaller than those between C and Cl, and C and H. That this is justified will be seen from the following calculations.

For CHCl, let $m_1=1$, $m_3=36$, $m_2=12$, $r_{12}=1.08\times10^{-8}$ cm, $r_{23}=1.8\times10^{-8}$ cm, $\alpha=110°$. Denoting the force constant between C and H by K_1, that between C and Cl by K_2, we have, from Eqs. (1),

$$\begin{aligned}&\nu_1^2+\nu_2^2+\nu_3^2=13/12\cdot K_1+K_2/9+0.496K_\alpha,\\&\nu_1^2\nu_2^2+\nu_2^2\nu_3^2+\nu_3^2\nu_1^2\\&\quad=0.1195K_1K_2+0.536K_1K_\alpha+0.526K_2K_\alpha,\\&\quad\nu_1^2\nu_2^2\nu_3^2=0.05625K_1K_2K_\alpha.\end{aligned}\tag{6}$$

Let us consider the Raman lines and the infrared data of *trans* $C_2H_2Cl_2$ in Table III. The selection rules require that frequencies active in Raman effect should be inactive in infrared and *vice versa*. As the frequencies of two vibrations of $C_2H_2Cl_2$ that differ only in the phase relation in the two CHCl groups should not be greatly different from each other, we can pick out the three pairs

$$\begin{cases}3072\text{ (Ra.)}\\3090\text{ (Inf.)},\end{cases}\quad\begin{cases}1271\text{ (Ra.)}\\1200\text{ (Inf.)},\end{cases}\quad\begin{cases}840\text{ (Ra.)}\\820\text{ (Inf.)}\end{cases}$$

as the only ones that can be reasonably ascribed to

$$\begin{cases}\nu_{\sigma s}\\\nu_{\sigma a},\end{cases}\quad\begin{cases}\delta_{\pi s}\\\delta_{\pi a},\end{cases}\quad\begin{cases}\nu_{\pi s}\\\nu_{\pi a}.\end{cases}$$

The differences between the two frequencies in each pair are due to the interaction between the two CHCl groups. Hence as an approximation we shall take the mean of the Raman and the infrared frequencies, namely, 3080, 1230, 830, as the three fundamental frequencies of CHCl. For the determination of the constants K_1, K_2, K_α, an exact assignment is immaterial, as ν_1, ν_2, ν_3 enter symmetrically in the above three equations. Solution of Eqs. (6) with $(\nu_1, \nu_2, \nu_3)=(3080, 1230, 830)$ gives

$$\begin{aligned}&K_1=5.17\times10^5\text{ dynes/cm},\\&K_2=4.01\times10^5\text{ dynes/cm},\\&K_\alpha=1.71\times10^{-11}\text{ dyne cm/radian}.\end{aligned}\tag{7}$$

The closeness of the value K_1 (CH) to that obtained from CH_2, namely 5.0×10^5, and the order of magnitude of K_α as compared with the deformation constants of all known triatomic systems[11] justified the valence force treatment.

To find the correspondence between the frequencies 3080, 1230, 830 and the three modes of vibrations ν_1, ν_2, ν_3 (Fig. 4), let us again study the relative dependence of these frequencies on K_α. One would expect ν_2 to depend most strongly on K, while ν_3 should be practically independent of K_α. From Eqs. (5), we have

$$\begin{aligned}&d\nu_i/dK_\alpha=\ 14\text{ cm}^{-1}/10^5\text{ dynes/cm},\quad\nu_i=\ 830,\\&d\nu_j/dK_\alpha=338\text{ cm}^{-1}/10^5\text{ dynes/cm},\quad\nu_j=1230,\\&d\nu_k/dK_\alpha=\ \ 1\text{ cm}^{-1}/10^5\text{ dynes/cm},\quad\nu_k=3080.\end{aligned}$$

The slight dependence of the frequency 3080 and the great dependence of the frequency 1230 show that $\nu_1=830$, $\nu_2=1230$, $\nu_3=3080$.

For CDCl, $m_3=2$ and the other data are the same as for CHCl. Eqs. (1) give

$$\begin{aligned}&\nu_1^2+\nu_2^2+\nu_3^2=7/12\cdot K_1+K_2/9+0.2815K_\alpha,\\&\nu_1^2\nu_2^2+\nu_2^2\nu_3^2+\nu_3^2\nu_1^2\\&\quad=0.064K_1K_2+0.163K_1K_\alpha+0.310K_2K_\alpha,\\&\quad\nu_1^2\nu_2^2\nu_3^2=0.01627K_1K_2K_\alpha.\end{aligned}$$

Table III. *Raman and infrared data of trans* $C_2H_2Cl_2$, $C_2D_2Cl_2$.

$C_2H_2Cl_2$						$C_2D_2Cl_2$	
Infrared	Raman			Assignment		Raman	
cm^{-1}	cm^{-1}	Int.	ρ	Trumpy	Wu	cm^{-1}	Int.
	350	(10)	0.29	$\delta_{\sigma s}$	$\delta_{\sigma s}$	346	(4)
620					$\delta_{\sigma' s}$		
	752	($\frac{5}{2}$)	0.70	$\delta_{\sigma' a}$	$\delta_{\sigma' a}$	657	(1)
820					$\nu_{\pi a}$		
	840	(3)	0.08	$\nu_{\sigma s}$	$\nu_{\pi s}$	765	(2)
917					torsion		
1200					$\delta_{\pi a}$		
	1271	(7)	0.20	$\delta_{\pi s}$	$\delta_{\pi s}$	992	(6)
	1575	(5)	0.08	$\nu_{2\pi s}$	$\nu_{2\pi s}$	1570	(6)
	1625	($\frac{1}{2}$)	p	$\delta_{\sigma s}+\delta_{\pi s}$	$\delta_{\sigma s}+\delta_{\pi s}$	1323	(0)
	1690	($\frac{1}{2}$)	p	$2\nu_{\sigma s}$	$2\nu_{\pi s}$	1540	(3)
	3072	(5)	0.20	$\nu_{\pi s}$	$\nu_{\sigma s}$	2325	(4)
3090					$\nu_{\sigma a}$		
	3140	($\frac{1}{2}$)	p	$2\nu_{2\pi s}$	$2\nu_{2\pi s}$	3150	(0)

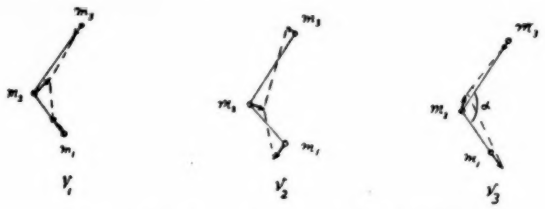

FIG. 4. Fundamental vibrations of CHCl.

With the values K_1, K_2 and K_α determined above for CHCl (Eq. (7)), solution of these equations gives

$$\nu_1=755, \quad \nu_2=960, \quad \nu_3=2320.$$

The closeness between these values and the Raman lines of *trans* $C_2D_2Cl_2$ found by Trumpy,[8] namely,

765, 992, 2325,

again show that the assignment of these frequencies is essentially correct, and that the valence force treatment of these CHCl, CDCl groups is satisfactory.

Va. *Trans* $C_2H_2Cl_2$

Let us consider the *trans* $C_2H_2Cl_2$. According to the selection rules in Table I, there should be five strong and polarized, one weak and depolarized Raman lines. These six Raman effect active frequencies are inactive in the infrared, while the other six Raman effect inactive frequencies are active in the infrared. The Raman spectra and infrared absorption data are summarized in Table III.

The classification of the Raman lines by Trumpy[8] is shown in the fifth column. In view of our calculations on CHCl and CDCl, the lines 3072 and 840 should be $\nu_{\sigma s}$ and $\nu_{\pi s}$, respectively. The Raman line 752 is probably $\delta_{\sigma' s}$ which should be completely depolarized and comparatively weak, although the value $\rho=0.70$ is a little too low for a completely depolarized line ($\rho=6/7$). The infrared bands at 820, 1200 and 3090 cm^{-1} have already been assigned to $\nu_{\pi a}$, $\delta_{\pi a}$ and $\nu_{\sigma a}$ in the above calculations. $\delta_{\sigma a}$, which one expects to be of the same order of, and in fact lower than $\delta_{\sigma s}$, lies in a region not covered in the work of Wu.[9] The vibration $\delta_{\sigma' a}$ and the torsional vibration are infrared active and there are two infrared bands at 620 and 917 cm^{-1}. If one assumes $\delta_{\sigma' s}>\delta_{\sigma' a}$ as in C_2H_4, then $\delta_{\sigma' a}=620$, torsional frequency $=917$. As the torsional frequency in C_2H_4 has been estimated at 745–800 cm^{-1} from specific heat data,[13] and as in *cis* $C_2H_2Cl_2$ $\delta_{\sigma' a}=694$, the assignment here is not unreasonable.

Vb. *Cis* $C_2H_2Cl_2$

In the case of *cis* $C_2H_2Cl_2$, there should be five strong and polarized ($\rho<6/7$) lines and seven weaker, completely depolarized ($\rho=6/7$) lines. The five strong Raman frequencies are active in infrared; the direction of the change of electric moment is along the axis of middle moment of inertia, and according to the consideration of Dennison[14] for the vibration-rotational band of an asymmetrical rotator, the band should possess no zero branch (type M). The four σ' vibrations, however, have their change of electric moment along the axis of least moment of inertia, and the vibration-rotational bands should possess a zero branch (type L). The vibration $\delta_{\sigma' a}$ corresponds to a change of electric moment along the axis of greatest moment of inertia and the band should also possess a zero branch (type G). Investigation, however, of the infrared spectrum[9] reveals only six intense absorptions at 570 (M), 694 (L or G), 857 (L), 1303 (L), 1591 (M) and 3087 (M). The band 3087 (M) has the corresponding strong, polarized Raman line at 3078; and according to our calculations on CHCl, it is $\nu_{\sigma s}$. The band

TABLE IV. *Raman and infrared data of cis* $C_2H_2Cl_2$, $C_2D_2Cl_2$.

$C_2H_2Cl_2$						$C_2D_2Cl_2$	
Infrared	Raman			Assignment		Raman	
cm^{-1}	cm^{-1}	Int.	ρ	Trumpy	Wu	cm^{-1}	Int.
	171	(9)	0.5	$\delta_{\sigma a}$	$\delta_{\sigma a}$	171	(6)
	407	(5)	0.84	$\delta_{\sigma s}$	$\delta_{\sigma s}$	368	(3)
570 M	560	($\frac{5}{2}$)	0.88	$\delta_{\pi s}$	?	515	($\frac{3}{2}$)
694 G					$\delta_{\sigma' a}$		
710	711	(7)	0.07	$\nu_{\sigma a}$	$\nu_{\pi s}$	689	(6)
	806	($\frac{1}{4}$)	d	$\nu_{\sigma s}$	$\delta_{\sigma' s}$		
857 L					$\nu_{\pi a}$		
	880	($\frac{1}{2}$)	p	$\nu_{\sigma a}+\delta_{\sigma a}$	torsion		
	1180	(5)	0.70	$\delta_{\pi s}$	$\delta_{\pi s}$	850	(3)
1303 L					$\delta_{\pi a}$		
1591 M	1586	(7)	0.08	$\nu_{2\pi s}$	$\nu_{2\pi s}$	1575	(6)
	1688	(2)	p	?	?	1507	(2)
3087 M	3078	(10)	0.31	$\nu_{\pi s}$	$\nu_{\sigma a}$	2325	(6)
	3158	($\frac{1}{4}$)	p	$2\nu_{2\pi s}$	$2\nu_{2\pi s}$	3150	(0)

[13] A. Eucken and A. Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).
[14] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

TABLE V. *Fundamental frequencies of cis and trans $C_2H_2Cl_2$.*

	cis $C_2H_2Cl_2$						*trans* $C_2H_2Cl_2$				
		Infrared		Raman				Infrared	Raman		
NOTATION	Sym.	cm^{-1}	envel. obs.	cm^{-1}	int.	ρ	Sym.		cm^{-1}	int.	ρ
$\nu_{\pi s}$	π'	711	*M*?	711	(7)	0.07	*S*	—	840	(3)	0.08
$\nu_{\pi a}$	σ'	857	*L*				*A*	820	—		
$\delta_{\pi s}$	π'			1180	(5)	0.7	*S*	—	1270	(5)	0.20
$\delta_{\pi a}$	σ'	1300	*L*				*A*	1200	—		
$\nu_{2\pi s}$	π'	1591	*M*	1586	(7)	0.08	*S*	—	1575	(5)	0.08
$\nu_{\sigma s}$	σ'						*S*	—	3072	(5)	0.20
$\nu_{\sigma a}$	π'	3087	*M*	3078	(10)	0.31	*A*	3090	—		
$\delta_{\sigma s}$	σ'			407	(5)	0.84	*S*	—	350	(10)	0.29
$\delta_{\sigma a}$	π'			171	(9)	0.5	*A*		—		
$\delta_{\sigma' s}$		—		806	$(\frac{1}{2})$	depol.		—	752	$(\frac{5}{2})$	0.70
$\delta_{\sigma' a}$		694	*G*					620	—		
Torsion		—		878	$(\frac{1}{2})$	pol.		917	—		

1591 (*M*) and the corresponding Raman line 1586 are evidently $\nu_{2\pi s}$. One expects to have a pair of frequencies at about 1200–1300 corresponding to the $\delta_{\pi s}$ 1270 (Ra), $\delta_{\pi a}$ 1200 (Inf.) of *trans* $C_2H_2Cl_2$. The infrared band 1303 (*L*) is probably the frequency $\delta_{\pi a}$ whose symmetry type is σ' and whose corresponding Raman line might have been too weak to be observed. The strong line 1180 cm^{-1} must then be ascribed to $\delta_{\pi s}$ although the degree of depolarization ($\rho = 0.70$) seems rather high. The line 711 cm^{-1}, being the only strong and polarized line in the neighborhood of 800 cm^{-1}, can be ascribed to $\nu_{\pi s}$. Its corresponding infrared band is not explicitly given in the paper, but the asymmetry and the great width of the absorption region at 694 cm^{-1} [9] compared with other bands suggest the existence of a band at about 710 cm^{-1}. The infrared band at 857 cm^{-1} has a zero branch and is most probably $\nu_{\pi a}$. The larger differences between $\nu_{\pi s}$ (711) and $\nu_{\pi a}$ (857), and between $\delta_{\pi s}$ (1180) and $\delta_{\pi a}$ (1303) than in the case of *trans* $C_2H_2Cl_2$ may be due to the larger interaction between the two CHCl groups in *cis* $C_2H_2Cl_2$. The completely depolarized line 407 is $\delta_{\sigma s}$ as Trumpy assumed, and the polarized line 171 ($\rho = 0.5$) is then probably $\delta_{\sigma a}$. The infrared band 694 cm^{-1} with a strong zero branch may be ascribed to $\delta_{\sigma' a}$, and the weak and depolarized line 806 can be ascribed to $\delta_{\sigma' s}$ as it is the only one near the corresponding frequency 752 in *trans* $C_2H_2Cl_2$. The torsional vibration should be active in Raman effect. If the assignment of the infrared band 917 in *trans* $C_2H_2Cl_2$ to its torsional vibration is correct, then it is reasonable to ascribe the weak line 878 to it, although its polarization character does not fit with the rule very well. It seems that all the observed strong Raman lines and infrared bands can be accounted for except the strong, completely depolarized line 561 and the infrared band at 570 cm^{-1} with no zero branch. The closeness between these two values shows that they are probably due to one single vibration. The theory requires that in *cis* $C_2H_2Cl_2$, an infrared band of the *M* type must appear as a strong and polarized Raman line, and a completely depolarized line must appear in the infrared with a zero branch. Thus these rules provide no place for the frequency in *cis* $C_2H_2Cl_2$, and hence the difficulty cannot be removed by changing the assignment alone.

The assignment of the fundamental frequencies is given in Tables IV and V.

Infrared Absorption Spectra of the Alcohols, Two Acids, and Their Solutions in Carbon Tetrachloride

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The paper describes the absorption spectra of the first eight alcohols of the aliphatic series and of formic and acetic acids in the regions extending from 0.9 to 2.2μ and from 2.0 to 4.0μ. The absorptions of the pure liquids are compared with their absorptions in carbon tetrachloride solutions. For methyl and ethyl alcohols and the two acids comparisons are also made with their vapor spectra. In every case solution in carbon tetrachloride modifies the bands characteristic of the hydroxyl group and leaves unchanged the hydrocarbon bands. The modifications are attributed to polymers or lattice structures which are partially destroyed in the solutions. Four bands near 0.96, 1.40, 1.89 and 2.1μ for the alcohols and one near 1.40μ for the acids which are present in the solution spectra are attributed to single molecules. Each of them in the solution spectra is accompanied by a broad almost continuous region of absorption on its long wave-length side, attributed to polymers, which grows stronger with increasing concentration until in the pure liquid it practically replaces the sharper bands predominating in the solution. The bands of the single molecules can still be detected, however, in each of the pure liquid alcohols. Comparison is made with the spectrum of aniline whose behavior near 1.4μ is peculiar.

THE work of several investigators[1-4] has shown that the spectra of liquid organic compounds containing the hydroxyl group undergo modification when these substances are dissolved in nonpolar solvents such as carbon disulfide and carbon tetrachloride. The most striking of the observed changes occurs in the 1.4μ overtone band of the hydroxyl group of the alcohols. The liquid alcohols possess in this region a very broad, almost continuous, absorption. When they are diluted with carbon tetrachloride a very strong and narrow band develops, for each alcohol, on the short wave-length side of the broad region, and the broad band itself grows weaker. The existence of these sharp bands in solutions 0.01 molar was first reported by Wulf and Liddell,[1] and they were used by these authors as a means of detecting the presence of hydroxyl groups. Several years ago, before the work of Wulf and Liddell had come to our notice, we began the study of this effect[2] in the region extending from 0.9 to 2.2μ, giving our attention to a comparison of the liquid absorption with the absorption produced by the carbon tetrachloride-alcohol mixtures, rather than to the absorption of the solutions themselves. The purpose of this paper is to present these comparisons for the alcohols and formic and acetic acids, and to indicate their bearing upon the phenomenon of molecular association in the liquid state. For purposes of comparison we have included records of the vapor absorption of methyl and ethyl alcohols, and of formic and acetic acids; and to make a comparison with the behavior of compounds containing the NH_2 group we have included records of the absorption of aniline.

Although the main points of the paper are concerned with the spectra obtained by means of the self-recording quartz spectrograph of the laboratory,[5] which extend from 0.9μ to 2.2μ, a series of absorption curves comparing the spectra of the liquids with the spectra of the liquids dissolved in carbon tetrachloride are given also for the region extending from 2.0 to 4.0μ obtained under the much smaller dispersion and resolving power of a small Hilger rocksalt spectrometer. For the region reached by the quartz instrument, slit widths were equivalent to about 0.003μ, and wave-length values are correct to within this accuracy.

The alcohols and the carbon tetrachloride were distilled, in many cases, several times either over calcium sulphate or magnesium perchlorate (anhydrone), and the middle fraction of constant boiling point was collected. The solutions consisted of one part by volume of the alcohol or acid and nineteen parts of carbon tetrachloride,

[1] Wulf and Liddell, J. Am. Chem. Soc. **57**, 1464 (1935).
[2] Kinsey and Ellis, Phys. Rev. **49**, 105 (1936).
[3] Freyman, Ann. de physique **20**, 243 (1933).
[4] Naherniac, Comptes rendus **200**, 1742 (1935).
[5] J. W. Ellis, Rev. Sci. Inst. **4**, 123 (1933).

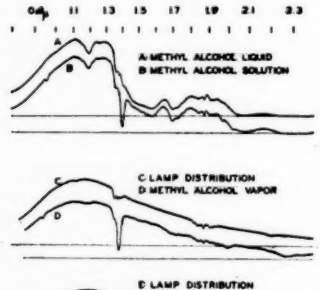

FIG. 1. Self-recorded transmission curves of the vapor, liquid, and CCl_4 solution states of methyl and ethyl alcohols; liquid cell thickness, 2 mm; solution cell thickness, 4 cm; concentration, 1 : 19 by volume; vapor cell thickness, 96 cm. Vapor approximately saturated at room temperature.

unless otherwise noted, and were contained in a cell 4 cm long. The liquids were contained in a cell 2 mm long so that the solution and liquid records of any one alcohol compare spectra produced by the same total mass of the absorber. Any differences between the spectra produced by the liquids and the solutions will therefore be caused by a change in the character of the molecules of the solute brought about by the solvent or by solvent-solute molecule perturbations. Because of the use of the 1 : 19 ratio for all the solutions the molar concentrations range from 1.0 molar for methyl to 0.3 molar for octyl alcohol.

ALCOHOL RECORDS, 0.9 TO 2.2μ

Figs. 1, 2 and 3 present original records of the transmissions of the first eight alcohols of the aliphatic series obtained by the quartz spectrograph. Galvanometer deflections are automatically recorded and are plotted against wavelengths in μ. The curves show, in addition to the transmissions of the pure liquids and the carbon tetrachloride-alcohol solutions, transmissions of the vapors of ethyl and methyl alcohols. Bands or groups of bands to which it is desired to direct attention lie at 0.96, 1.15, 1.40–1.65, 1.70, 1.89, and 1.95–2.1μ, and can be seen easily in the figures. Comparisons of the liquid and solution spectra show that the four of these which lie at 0.96, 1.40–1.65, 1.89, and 1.95–2.1μ are strongly modified by solution in carbon tetrachloride and that the two at 1.15 and 1.70μ, which are definitely known to be produced by vibrations characteristic of the hydrocarbon groups, are not.

The bands at 1.40 and 0.96μ are undoubtedly the first and second overtones of the fundamental characteristic of the hydroxyl group which lies near 3μ. The 0.96μ band escapes detection in the liquid spectrum and appears as a fairly sharp but weak band in the solution lying at the same wavelength for all the alcohols. Freyman,[3] and later Naherniac,[4] have studied it in the liquid in thicker cells and in carbon tetrachloride solutions

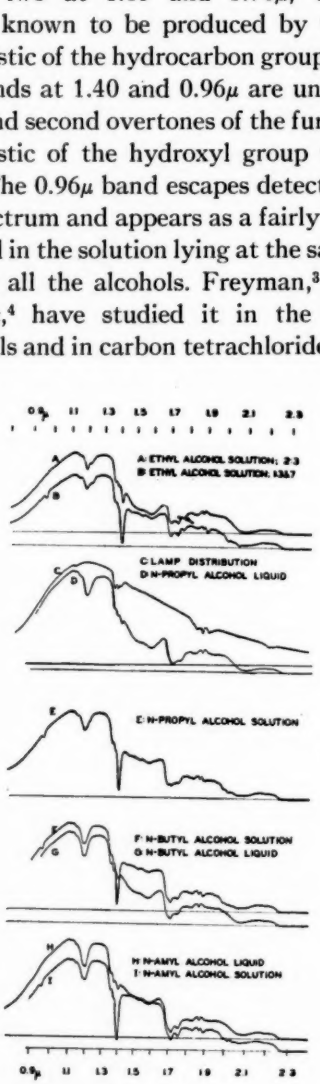
A: ETHYL ALCOHOL SOLUTION; 2:3
B: ETHYL ALCOHOL SOLUTION; 1:35.7
C: LAMP DISTRIBUTION
D: N-PROPYL ALCOHOL LIQUID
E: N-PROPYL ALCOHOL SOLUTION
F: N-BUTYL ALCOHOL SOLUTION
G: N-BUTYL ALCOHOL LIQUID
H: N-AMYL ALCOHOL LIQUID
I: N-AMYL ALCOHOL SOLUTION

FIG. 2. Self-recorded transmission curves for: *A*, 5 mm cell of a 2 : 3 by volume CCl_4 solution of ethyl alcohol; *B*, 7.5 cm cell of a 1 : 35.7 by volume CCl_4 solution of ethyl alcohol; *D* to *I*, liquid and solution states of propyl, butyl, and amyl alcohols in cell lengths of 2 mm for the liquid, 4 cm for solution.

as a function of the concentration. It appears in ethyl and methyl alcohol vapors at 0.948μ.

The 1.40μ region presents features of the greatest interest. As we have mentioned, the broad absorption band so characteristic of the liquid spectrum of all the alcohols, and which stretches almost like a continuous spectrum (with some structure) from about 1.4 to 1.65μ, is considerably weakened in the solution spectrum and is accompanied on its short wave-length edge by a sharp band at 1.408μ which occurs at this same position in the eight alcohols examined. In every case the sharp band is feebly present at the same position in the liquid spectrum. In methyl and ethyl alcohol vapors it occurs at 1.387μ and 1.395μ, respectively. When the alcohols are diluted the broad band of the liquid spectrum, which appears to be double, develops sharper structure, the main features of which are strikingly similar although not exactly alike for all the alcohols.

The band at 1.89μ falls in a region where the galvanometer deflections are small and in the midst of a band at 1.87μ produced by the absorption of the water vapor which was always present in the light path of the spectrograph. Its position in the solution at 1.895μ is the same for all the alcohols. A careful inspection of the plates shows that it occurs in the spectra of all the solutions, but is absent from the pure liquid records. In these it is replaced by what appears to be a broad continuous absorption on the long wave-length side of its position in the solution spectrum.

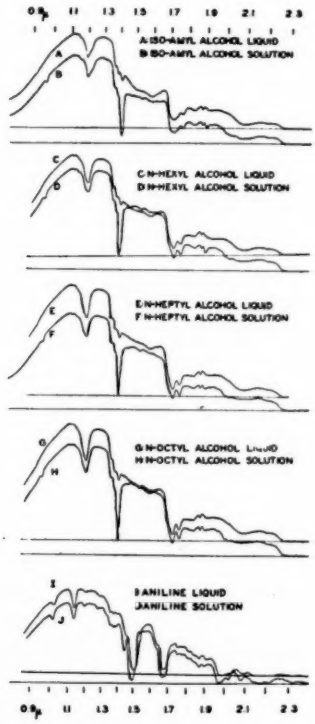

FIG. 3. Self-recorded transmission curves for alcohols from amyl to octyl and for aniline, in liquid and CCl_4 solution states. Liquid cell thickness, 2 mm. Solution (1 : 19 by volume) cell thickness, 4 cm.

In the 1.95–2.1μ region the same change in the spectrum in passing from liquid to solution occurs. The broad continuous region develops structure and deeper bands on its short wave-length side and becomes weaker toward long wave-lengths.

To show these features more clearly the liquid and solution records for heptyl alcohol, which were chosen as typical of the behavior of the eight alcohols, have been reduced, with the help of the background distribution curve, to give percent transmissions. These were obtained, for the solution, by allowing the radiation to traverse pure carbon tetrachloride contained in the same 4 cm cell which was used for the solution records. The ordinates of the background curve were multiplied by a factor, nearly unity, which was selected to adjust the deflection of the background curve equal to the deflection of the solution curve at a position of the spectrum free from the absorption of the alcohol. Ordinates were measured at intervals of 0.5 mm across the plate, that is at approximately every 0.003μ. In the reduced curves (Fig. 5) the percent transmissions are plotted against plate scale readings which may be converted into wave-lengths by means of the dispersion curve of the instrument, also given in the figure. The wave-length values for the dispersion curve are plotted vertically on the right. The behavior of the broad band of the liquid spectrum at 1.4μ and of the bands at 1.89 and 2μ perhaps can be followed more clearly in these records. The broad band at 1.4–1.65μ in the solution has four components, each of which occurs in the spectra of the other alcohols.

Discussion of the Alcohol Spectra

It seems to be generally agreed that the changes in the absorption spectra of the alcohols

which are brought about by solution in carbon tetrachloride are caused by the dissociation of polymers which exist in the liquid state, or if definite polymers do not exist, by the weakening of the effects of a liquid lattice which solution in carbon tetrachloride would undoubtedly produce. The sensitivity of the two bands at 0.96 and 1.4μ, which are characteristic of the hydroxyl group, to dilution with a nonpolar solvent, and the absence of a corresponding effect in the bands known to be characteristic of the hydrocarbon groups confirm the belief that the aggregates are held together by forces which arise mainly between the polar hydroxyl groups, and which have little effect upon the hydrocarbon part of the molecule. The existence of the two bands at 0.96μ and 1.40μ in the vapor shows that these are probably characteristic of a single unperturbed molecule. The occurrence of the broad absorption which can be attributed to polymers on the long wave-length side of the 1.40μ band in the solutions along with the sharp band due to single molecules shows that at the dilutions used polymers still exist in considerable concentration. On the other hand, the occurrence of the sharp band at 1.4μ in the liquids (more pronounced in the higher alcohols) indicates that the liquids themselves are mixtures of free and polymerized molecules. The alteration which solution in carbon tetrachloride produces in the bands characteristic of the hydroxyl group may be used, with some caution, to detect bands characteristic of this group. The band at 1.89μ which appears only in solution (see solution curve for heptyl alcohol, scale reading 25.20, Fig. 5) is therefore likely to be a "hydroxyl" band. A band that corresponds to the water band which is observed in this region would be expected near this position if the alcohols, like water, possessed characteristic frequencies near 6.1μ; for it would be (as it is for water) the combination band ($\sigma+\delta$) formed from the 3 (σ) and 6.1μ (δ) fundamentals. Although the absorption curves of Weniger[6] show absorption bands near 6μ, unlike those for water, they are very weak. Moreover, the 6.1μ or δ vibration of water is associated with a change in the angle between the two hydrogen-oxygen bonds and therefore, having as its counterpart in an alcohol an oscillation of the oxygen-hydrogen bond relative to a bond between an oxygen and a hydrocarbon group, it would involve forces of a different nature and would not be comparable to this type of vibration in an alcohol. Nevertheless, the fact remains that a band at 1.89μ occurs in all the alcohols which is altered by dilution with carbon tetrachloride and is unaffected by the length of the hydrocarbon chain, so that, like the 0.96 and 1.4μ bands to which in these respects its behavior is similar, it will be regarded as characteristic of the hydroxyl group.

The 1.95–2.1μ band is unique among those which are affected by dilution because it is the only one which appears to be considerably affected by the length of the hydrocarbon chain. For methyl alcohol it is also the only one which has a different character in the solution than it has in the vapor. It is likely that it is a combination band formed by an intercombination of hydroxyl and hydrocarbon frequencies.

The effect of polymerization or lattice formation in the liquid on the hydroxyl bands of single molecules then is to destroy them and produce on their long wave sides broad and almost continuous absorption. This absorption is most pronounced between 1.4 and 1.65μ, and occurs unmistakably near 1.89 and 2.1μ. There is a definite suggestion of it on the long wave-length side of the weak 0.96μ band. The polymer band at 1.4–1.65μ shows four distinct minima which can be found in the records of the solutions of all eight alcohols. Feeble bands in this region appear also in the vapor spectra of ethyl and methyl alcohols, a fact which indicates that the vapors are partially polymerized.

The features exhibited by the fundamental bands of the 3μ region are not inconsistent with the behavior of the bands in the overtone region described in the previous paragraphs. Absorption spectra of the eight alcohols in the liquid and solution state were obtained for us by Mr. Waldo Lyon, by means of a small Hilger rocksalt instrument. The resolution and dispersion were poor and the slit width, corresponding to 0.05μ, was large compared to the width used in the overtone region. The transmission curves for the liquid and solution states (Fig. 6) show the two transmission minima that correspond to the hydroxyl and hydrocarbon characteristic frequencies. They lie at 2.95 and 3.45μ, respectively,

[6] W. Weniger, Phys. Rev. **31**, 388 (1910).

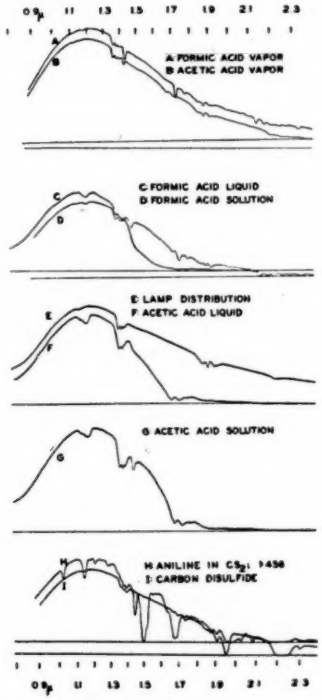

FIG. 4. Self-recorded transmission curves for: *A* to *G*, the vapor, liquid, and CCl_4 solution states of formic and acetic acids, cell lengths 2 mm for liquids, 4 cm for solutions. Solution concentration, 1 : 19 by volume for acetic acid; saturated solution for formic acid. Vapor, saturated at room temperature. *H*, *I*, aniline in CS_2, 1 : 456 by volume, and CS_2, cell lengths, 96 cm.

in the solution spectrum, and in the liquid are displaced toward longer wave-lengths. In addition, the hydrocarbon band appears considerably broadened in the liquid. This shift and change in character of the hydrocarbon band is, however, only apparent. The broad polymer absorption that may be expected in this region corresponding to its overtone in the 1.4μ region should be sufficiently strong to sweep over the hydrocarbon band, especially for the slit width used. The length of the absorbing cell of the liquid alcohol, which was about 0.01 mm, was so small that it could not be controlled to keep the product of concentration and cell length the same for the solution and liquid cases as accurately as it could be for the longer cells which were used in the overtone region. Some variation therefore in the hydrocarbon band in passing from solution to liquid may be expected from this cause.

Errera and Mollet[7] have recently obtained the strong band expected in this region in solutions of the alcohols in carbon tetrachloride as dilute as 0.1 molar. It is clear therefore that in this region the spectra of the solutions which we studied are not characteristic of the single molecules. The band at 2.95μ is largely produced by polymer absorption which masks the sharp band found by Errera and Mollet at 2.75μ—the fundamental of the sharp overtone at 1.4μ.

The vapor absorption of methyl and ethyl alcohols in this region (Fig. 6, curves *C* and *D*) also is evidently not entirely due to single molecules; for although the vapor bands resemble those of the solution much more than they do those of the liquid, the hydroxyl transmission minimum falls at 3μ, the position of maximum absorption of the polymer band found by Errera and Mollet, and not at 2.75μ, the position of the band presumably produced by single molecules. The vapors of methyl and ethyl alcohols appear therefore to be partially polymerized. To what extent this is so it is not possible to say on the basis of these records. There is good indication from Errera and Mollet's absorption curves that the hydroxyl absorption probabilities for the associated state are very large compared to those for the single molecules, so that strong absorption in the polymer region relative to the absorption due to single molecules will not necessarily indicate a large proportion of polymers. This is shown by the enormous increase in the polymer absorption and the corresponding small decrease in the single molecule absorption at 2.75μ which, Errera and Mollet found, occurs in 0.1 molar solutions when the temperature is lowered from 70° to 0°. We have observed this same temperature effect for the solution bands in the 1.4μ overtone region.

FORMIC AND ACETIC ACIDS. ANILINE

We have compared also the absorption of formic and acetic acids in the liquid, solution and vapor states to see whether any of the features which the spectra of the alcohols present are present also in the acid spectra.* Acid transmissions in the 0.9 to 2.2μ region are shown in Fig. 4. The transmissions for the liquid and

[7] Errera and Mollet, Nature **138**, 882 (1936).

* For a discussion of polymer bands in acetic acid vapor from 3 to 10μ the reader is referred to a paper by Gillette and Daniells, J. Am. Chem. Soc. **58**, 1139 (1936).

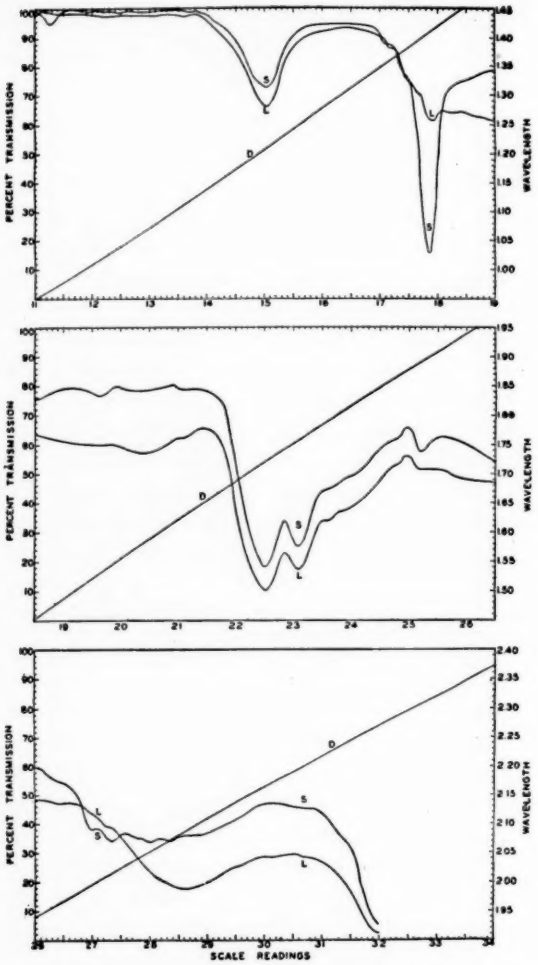

FIG. 5. Percent transmissions for (*L*) liquid heptyl alcohol, and (*S*) CCl_4 solution of it (1 : 19 by volume). Liquid cell length, 2 mm; solution cell length, 4 cm. *D*, dispersion curve of spectrograph.

solution states of acetic acid at 3μ are shown in Fig. 6 by curves *A* and *B*. The concentrations of formic and acetic acid solutions (1 : 19 by volume) were 1.3 and 0.8 molar, respectively. In the liquid a broad region of continuous absorption begins near 1.4μ and extends to opacity toward longer wave-lengths. In the carbon tetrachloride solutions this absorption is weakened and is accompanied on its short wave-length edge by the sharp hydroxyl band. The sharp band also occurs in the vapor, but the continuous absorption has been greatly reduced. The continuous absorption in the cell lengths used was so strong that it masked completely the 1.89 and 2.1μ regions in which bands were found for the alcohols. The weakness of the sharp 1.4μ overtone band relative to its intensity for the alcohols accounts for the absence of a second overtone corresponding to the alcohol band at 0.96μ. In the 3μ region acetic acid behaves like the alcohols. The broad continuous absorption of the liquid is reduced but not extinguished in the solution.

It is interesting to compare this behavior with the behavior of a substance like aniline, which contains the NH_2 group. Curves *I* and *J* of Fig. 3 show the absorption of 2 mm of liquid aniline and 4 cm of a solution of it in CCl_4 (1 : 19 by volume, 0.5 molar). Curve *H*, Fig. 4, shows the absorption of 96 cm of a dilute solution in carbon disulfide (1 : 435 by volume, 0.03 molar). The liquid and solution spectra are very similar except in one striking feature. The two bands at 1.45 and 1.495μ reported by Wulf and Liddell to be characteristic of the NH_2 group in carbon tetrachloride solution appear, but in the liquid the short wave-length component is reduced to a mere shoulder of the other component which remains with its intensity unaltered. Both bands,

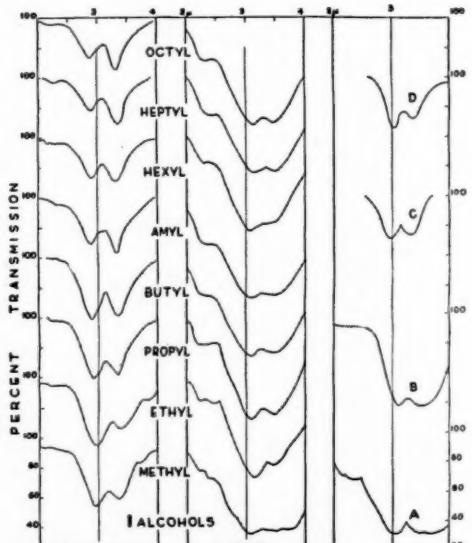

FIG. 6. Left, percent transmissions for liquid and solution states of the alcohols. Liquid cell length, 0.01 mm. Solution (1 : 19 by volume) cell length, 0.2 mm. Right, percent transmissions for: *A*, 0.01 mm cell liquid acetic acid; *B*, 0.2 mm CCl_4 solution of acetic acid (1 : 19 by volume); *C*, 1 cm cell of methyl alcohol vapor; *D*, 1 cm cell ethyl alcohol vapor. Vapor approximately saturated at room temperature.

however, are slightly shifted in position. The long wave-length component has a shoulder on its long wave-length side which is more pronounced in the solution than in the liquid. But there is no broad absorption, so characteristic of the alcohols and acids, which is sensitive to dilution with carbon tetrachloride.

It appears therefore that the broad bands of the two acids, like the corresponding bands of the alcohols, are due to a coupling in the liquid state between the hydroxyl parts of the molecules. Since the coupling is very likely of the hydrogen or hydroxyl bond type recently discussed by Bernal and Megaw,[8] a study of these bands may make possible an experimental distinction between the two types of bonds. But if a distinction lies, as Bernal and Megaw suggest it does, in the absence of a characteristic hydrogen vibration in the hydrogen bond and, correspondingly, in its presence in a hydroxyl bond, the similarity of the spectra of the alcohols and acids shows that their bondings are alike.[9] And certainly not enough is known about these bonds to say that the apparently greater strength or wider range of the acid polymer bands is sufficient to distinguish between a hydrogen bond in which a proton interchange between oxygens can take place and a hydroxyl bond in which it cannot. For the present the infrared evidence supports the view that, with respect to the behavior of hydrogen, the alcohol and acid polymer bonds are alike.

[8] Bernal and Megaw, Proc. Roy. Soc. **A151**, 384 (1935).

[9] Compare, for example, Bernal and Megaw's remarks on acetic acid (reference 7, page 420) in which they use the absence of observed Raman lines caused by characteristic hydroxyl frequencies to indicate the presence of a hydrogen bond as distinct from a hydroxyl bond. The same argument based on the evidence of infrared absorption would lead to no such distinction in type between the alcohol and acid liquid lattice bonds.

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The Potential Function of the Water Molecule

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For use with frequencies corrected for anharmonicity the energy of a molecule is expressed by a complete quadratic form. Reduction of the force constants in Cartesian coordinates to an independent set by relations due to symmetry and mutual forces is carried out by a systematic matrix method which is particularly useful in correcting for anharmonicity and for finding functions of the frequencies and masses invariant in isotopic molecules. For H_2O and D_2O these relations being satisfied, the potential function is indeed assumed to be unchanged, all constants are computed, and compared with those of various models. In the $S-P_{\lambda}$ picture of the H_2O molecule the H−H repulsion, ionic terms in OH bonding and exchange integrals in the angular function prove to be the values expected theoretically.

A LARGE number of experimentally determined vibrational levels have been roughly correlated by the use of potential functions of simple models, but satisfactory agreement necessitates the use of a complete potential function. The spectra of a single molecule usually do not yield enough independent data to evaluate all the necessary constants. The many attempts at choosing functions with as many constants as frequencies are by definition only approximations; cross terms have to be neglected which often turn out to be large. It would be possible to determine all constants by substitution of isotopes provided the potential energy remains unchanged. There are enough experimental data for H_2O and D_2O to test whether the isotope makes significant changes in the potential function relative to the vibrational levels, and if not, to determine all the constants of a general quadratic potential expression for energy. It is instructive to evaluate the true values of cross terms of various models showing that it needs an intuitive choice very close to normal coordinates

* National Research Fellow in chemistry. The author is greatly indebted to Professor W. V. Houston of C. I. T. for his help in the preparation of this and the succeeding papers.

before the neglect of such terms does not affect low frequencies. It is also shown that as regards correlation with the S−P structure it is useless to calculate cross terms without proper correction for anharmonicity.

The isotope effect on vibrational levels will be investigated in two steps; first the classical frequencies at the bottom of the potential bowl will be determined using a complete quadratic expression, then anharmonicity corrections will be calculated from higher terms. For triatomic molecules the first step, that of changing to normal coordinates, has already been presented in many forms, but we shall take the opportunity to outline a method which works well for more complicated molecules, leading to formulae of "invariants" that can be used for the identification of bands and for the accurate prediction of the isotope effect. On replacing an atom by an isotope each vibrational frequency will not in general be multiplied by an "isotope factor" (function of masses only) unless it is alone in a representation; rather there will be factors by which certain invariants will change. Formulae of this sort are useful since they are quite accurate when applied to the observed frequencies, because unknown anharmonicity corrections largely cancel.

Frequencies When the Energy is a Complete Quadratic

Since we do not intend to neglect any constants there is no need to choose unusual coordinates. Simple Cartesian coordinates x_i for each atom are the clearest, and the corresponding constants will then be easily visualized and more easily interpreted than those resulting from an exotic choice of special coordinates. The simplifications of common sense and, in more complicated cases, of intuition are introduced as a straightforward algebraic formulation of group theory.

Let v_{ij} and t_{ij} be the constants in the bilinear forms for the potential and kinetic energies of an N atomic molecule

$$-2V=\sum_{ij} v_{ij}x_i x_j, \tag{1}$$

$$2T=\sum_{ij} t_{ij}\dot{x}_i\dot{x}_j, \tag{2}$$

summed from $i, j=1$ to $3N$ so that

$$v_{ij}=-\frac{\partial^2 V}{\partial x_i \partial x_j}$$

and $V=\|v_{ij}\|$ is symmetrical.[1]

The classical problem can be formulated as a diagonalization process to which the simplifications of group theory are most easily applied. The Lagrangian equations are

$$\sum_i (t_{ij}\ddot{x}_j+v_{ij}x_j)=0 \tag{3a}$$

and if harmonic motion of frequency ω is assumed, these reduce to

$$\sum_j v_{ij}x_j=\lambda\sum_j t_{ij}x_j, \quad \lambda=\omega^2. \tag{3b}$$

If $q^{(\lambda)}$ be a vector whose elements are the amplitudes of simple harmonic oscillation, in a normal coordinate, with frequency ω, the above set of $3N$ linear Lagrangian equations can be written as one,

$$T^{-1}Vq^{(\lambda)}=Dq^{(\lambda)}=\lambda q^{(\lambda)}, \tag{3c}$$

in which T and V are the matrices of the bilinear forms (1) and (2), and $T^{-1}V=D$. A matrix Q is defined whose columns are the $3N$ vectors $q^{(\lambda)}$, and Λ as a diagonal matrix whose elements correspond to the $3N$ λ's, any one of which satisfies (3b). The frequencies and amplitudes (coefficients of the linear transformation equations to normal coordinates) will be found by solving the matrix equation

$$Q^{-1}DQ=\Lambda, \tag{3d}$$

which is shorthand for the $3N$ sets of $3N$ linear equations (3c). Given D the problem is to find the matrix of transformation to normal coordinates Q, and the set of frequencies Λ. On the other hand, in our present state of knowledge, D is the unknown.

The frequencies Λ may or may not be all measurable, and since as yet the amplitudes Q are unobserved, D, hence V, cannot be calculated from the experiment, except in the few special cases where the number of independent ele-

[1] When there is degeneracy, as in a triatomic molecule of D_{3h}, it is convenient to use complex numbers. In that case the words "symmetrical" and "orthogonal" occurring below must be replaced by "Hermitian" and "unitary."

ments in D equals the number of observed frequencies, unless certain frequencies of one or more isotopic molecules with identical V's are known. To do this it is convenient to simplify (3d) to equations in independent constants, which is done in two steps of partial diagonalization. The number of different elements may be reduced by Cauchy relations, resulting from symmetry. If the molecule is not in a force field six roots λ corresponding to rotation and translations will be zero. The rank of the $3N$th order matrix is thus $3N-6$; hence there are 6 relations between the constants entirely different from those resulting from symmetry.

By a simple device the problem can be reduced to the diagonalization to Λ of a symmetrical matrix, requiring only an *orthogonal* transformation S which is much easier to work with than Q. In analogy to the usual treatment of reducing the bilinear expression for the kinetic energy to the canonical form, take $L^2=T^{-1}$ and $S=L^{-1}Q$ and substitute in (3d)

$$S'(LVL)S=\Lambda. \tag{4}$$

The matrix $D^{(1)}=LVL$ is symmetrical and has the same roots as D. If Cartesain coordinates were chosen T and L are diagonal, $l_i=1/\sqrt{m_i}$, and $d_{ij}^{(1)}=v_{ij}/(m_im_j)^{\frac{1}{2}}$.

If there is any symmetry partial diagonalization to blocks, each one referring to all oscillations of the same symmetry type, can be accomplished by a change of coordinates which can be picked so that the matrix of transformation has elements independent of the actual values of the potential constants. Such "symmetry coordinates" are often obvious, but in complicated cases when intuition is not developed enough, they can be deduced by group theory.

Let G be a matrix induced in configuration space by one of a group of symmetry operators. For example in Fig. 1 a rotation of π about the symmetry axis z (operator $C_2(z)$) induces

$$G(C_2z)=\begin{Vmatrix}\cos\pi & \sin\pi\\ -\sin\pi & \cos\pi\end{Vmatrix}\times\begin{Vmatrix}1&0&0\\0&0&1\\0&1&0\end{Vmatrix} \tag{5}$$

where the order of coordinates is $z_1y_1z_2y_2z_3y_3$: the first matrix is the usual rotation of coordinates,

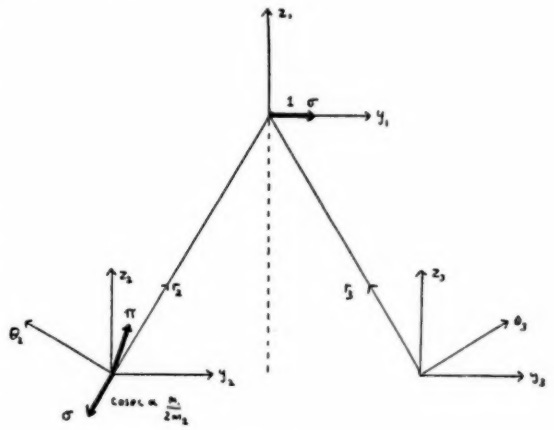

FIG. 1.

and the second the permutation of the atoms. Such an operation merely changes the phase of a characteristic oscillation $q^{(\lambda)}$ so that

$$Gq^{(\lambda)}=\gamma q^{(\lambda)}, \tag{6}$$

where γ is a root of unity. In the case of degeneracy $q^{(\lambda)}$ has to be properly chosen from the infinite set of degenerates $q^{(\lambda)}$'s to satisfy (6).

The diagonalization to blocks is done by a unitary matrix R of columns $r^{(i)}$ which will reduce G (preferably the most complicated one) to a diagonal form, $\|\gamma_{ii}\|$ where γ_{ii} are roots of unity since G is always unitary. The matrix R will reduce all the matrices of the group if and only if there is no degeneracy.

$$Gr^{(i)}=\gamma_{ii}r^{(i)}. \tag{7}$$

Comparing (7) and (6) $q^{(\lambda)}$ is a linear combination of columns of R belonging to the same γ or representation, the coefficients of this combination being determined only by the force constants and not by symmetry. The elements in a column of R may be pictured as amplitudes of an oscillation of the system which has the correct symmetry properties: obviously a normal vibration is a linear combination of all such simply constructed modes *that have the same symmetry*. For a triatomic molecule belonging to D_{3h} the transformation R deduced as above by diagonalizing either the operator C_3 or S_6 is actually the required transformation to normal coordinates, $R\equiv S$: the diagonalization is complete. In general, by the introduction of symmetry

coordinates, as defined by R, the matrix

$$D^{(2)}=R'D^{(1)}R=D^{(2)(\Gamma_1)}\dot{+}D^{(2)(\Gamma_2)}\dot{+}\cdots \quad (8)$$

is divided into main diagonal blocks $D^{(2)(\Gamma_i)}$, one for each representation Γ_i. In the case of a triatomic molecule of symmetry C_{2v} the matrix R is

$$R=\frac{1}{\sqrt{2}}\begin{Vmatrix}\sqrt{2} & 0 & 0\\ 0 & 1 & 1\\ 0 & 1 & -1\end{Vmatrix}\times\begin{Vmatrix}1 & 0\\ 0 & 1\end{Vmatrix}, \quad (9)$$

when the order of coordinates is $y_1z_1y_2z_2y_3z_3$. The columns and rows of $D^{(2)}$ are then distributed among the representations in the same way as columns of R are, in this case $B_2A_1B_2A_1A_1D_2$. Symmetry is enforced on D by putting all non-diagonal blocks of $D^{(2)}$ identically zero, to give all the (Cauchy) relations between the v_{ij}'s that can be obtained from symmetry considerations, which relations are substituted in the main diagonal blocks. Since L commutes with R, $L^{-1}D^{(2)}L^{-1}$ is the matrix of force constants to be used with symmetry coordinates, of which many are still dependent.

Independent constants are now obtained by considering only mutual forces between the atoms, i.e., by removing rotations and translations. Algebraically this corresponds to knowing the roots λ for the latter are zero. This is not so if the molecule is in a force field, such as in a liquid or crystal lattice, in which case no further reduction beyond symmetry is possible. Since rotations and translations belong to definite representations each block $D^{(2)(\Gamma_i)}$ can be treated separately: indeed for simplicity different coordinates may be used in different blocks. It is easy to write down the $q^{(\lambda)}$'s for these motions of zero frequency, e.g., that for translation parallel to the axis of symmetry is $\sim(0\,1\,0\,1\,0\,1)$. Vectors $f^{(\lambda)}$ representing the amplitudes in symmetry coordinates are made from these

$$f^{(\lambda)}=R'L^{-1}q^{(\lambda)}. \quad (10)$$

For representation Γ_i a unitary matrix $F_{(\Gamma_i)}$ is set up with a column $f^{(\lambda)}$ for each rotation and translation belonging to that representation, the remaining columns being chosen as simply as possible to complete F and make it unitary. In our example

$$F(A_1)=\begin{Vmatrix}(m_1/M)^{\frac{1}{2}} & (2m_2/M)^{\frac{1}{2}} & 0\\ (2m_2/M)^{\frac{1}{2}} & -(m_1/M)^{\frac{1}{2}} & 0\\ 0 & 0 & 1\end{Vmatrix}, \quad (11)$$

$$M=m_1+2m_2.$$

The matrices (one for each representation)

$$D^{(3)(\Gamma_i)}=F'(\Gamma_i)D^{(2)(\Gamma_i)}F(\Gamma_i) \quad (12)$$

now contain the simplest possible set of independent mutual force constants and reduced masses, and of course have the same roots as the original D. They have a main diagonal block of order equal to the number of true vibrations in Γ_i, the remainder of the matrices being zero.

To summarize, a change of coordinates x_i to reduced mass symmetry coordinates ξ_i has been made in configuration space,

$$x_i=q_{ij}\xi_j, \quad (13)$$

$$\|q_{ij}\|=Q=LRF, \quad (14)$$

where the transformation L was made to make the dynamical matrix D symmetrical, so that all subsequent transformations could be orthogonal: the change R divided the problem into separate representations, and F gave mutual forces, that is, coordinates fixed relative to the center of gravity. The last two are not commutative, but the first two are.

Application to the Molecule AB_2 of C_{2v}

For representation B_2, $D^{(2)}(B_2)$ is of the third order. Two columns of $F(B_2)$ belong to a rotation and a translation: hence the third is fixed and corresponds to the relative amplitudes of motion in the σ vibration. Contrary to many published diagrams, in the σ vibration atoms 2 and 3 always move along the bonds, and atom 1 perpendicular to the symmetry axis, and the relative amplitudes are functions of the masses and angles only. The ratio of the electric moments of isotopic molecules is a function only of the masses.

Since F is uniquely determined the diagonalization is complete,

$$D^{3}_{(\Gamma\mathfrak{l})}=\begin{Vmatrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & \lambda_\sigma\end{Vmatrix}. \qquad (15)$$

Equating (15) element for element we get in a very simple way the relations between the v_{ij}'s necessary to keep the center of gravity stationary and to prevent rotation, i.e., the mutual force constants. From these the trace comes out to be

$$\lambda_\sigma=\left(\frac{2\sin^2\alpha}{m_1}+\frac{1}{m_2}\right)(v_{r_2r_2}-v_{r_2r_3}). \qquad (16)$$

This is an expression of the same form as obtained previously for specialized models. Using *all* the terms of a quadratic potential function the only modification is in the force constant, which is neither that of the diatomic molecule AB nor that of a diatomic molecule AB with the same electronic structure as in AB_2, for as will be shown in (31) it contains a component of the interaction of atoms 2 and 3. As is the case with any frequency alone in a representation the force constants and masses occur in separate factors. The ratio of frequencies of any isotopic molecules, retaining the symmetry, is a function of the masses and angle only (the superscripts H and D refer to two isotopes of B)

$$\frac{\omega_\sigma{}^H}{\omega_\sigma{}^D}=\left(\frac{2\sin^2\alpha}{m_1}+\frac{1}{m_2{}^H}\right)^{\frac{1}{2}}\Big/\left(\frac{2\sin^2\alpha}{m_1}+\frac{1}{m_2{}^D}\right)^{\frac{1}{2}}. \qquad (17)$$

This formula and (18) have been shown before; here we show they are true for the general quadratic, and hence for a general potential function provided frequencies corrected for anharmonicity are used. In the case of H_2O the right-hand side has a value of 1.3647 using an angle[2] of 104° 41′. With the observed frequencies corrected for anharmonicity as described below the ratio is 1.3632.

A satisfactory agreement of the observed ratio to (17) shows that very probably the force constant $v_{r_2r_2}-v_{r_2r_3}$ is the same in the isotopic molecule. Assuming this we can use (17) to calculate the angle from the two observed frequencies.

$$\sin^2\alpha=\frac{m_1}{2}\left(\frac{\lambda_\sigma{}^D}{m_2{}^H}-\frac{\lambda_\sigma{}^H}{m_2{}^D}\right)\Big/\lambda_\sigma{}^H-\lambda_\sigma{}^D, \qquad (18)$$

which gives $2\alpha=107°\ 22'$ in fair agreement with the angle obtained from rotational analysis,[2] 103° 20′ to 107° 20′. The formula (18) is very sensitive to the frequencies, and the σ vibration of D_2O has not been measured under high resolution.

In the symmetrical representation A_1 the third-order matrix has rank two since one root belonging to translation parallel to the symmetry axis is zero. Using yz coordinates a simple $F(A_1)$ can be found removing this motion, reducing $D^{(3)}(A_1)=F(A_1)D^{(2)}(A_1)F(A_1)$ to a second-order matrix whose roots are λ_π and λ_δ.

$$D^{(3)}(A_1)=\frac{1}{m_2}\begin{Vmatrix}\mu^2 z_+ & -\mu w_-\\ -\mu w_- & y_-\end{Vmatrix}, \qquad (19)$$

where $z_+=v_{z_2z_2}+v_{z_2z_3}$, $w_-=v_{y_2z_2}-v_{y_2z_3}$,
$y_-=v_{y_2y_2}-v_{y_2y_3}$, $\mu=(M/m_1)^{\frac{1}{2}}$.

Further diagonalization depends on the actual force constants. It turns out that for this molecule transformation to $r\theta$ coordinates (Fig. 1) reduces the nondiagonal element enough to neglect it relative to the larger root λ_π. However, without numerical knowledge of the force constants, the possible affect of isotope on them can be tested. From the determinant of (19)

$$\lambda_\pi\lambda_\delta=(M/m_1m_2{}^2)(z_+y_--\omega_-{}^2), \qquad (20)$$

so that

$$\frac{\omega_\pi{}^H\omega_\delta{}^H}{\omega_\pi{}^D\omega_\delta{}^D}=\frac{m_2{}^D}{m_2{}^H}\left(\frac{M^H}{m^D}\right)^{\frac{1}{2}}, \qquad (21)$$

a function independent of angles or internuclear distances. For H_2O-D_2O it is 1.895. With Bonner's frequencies[3] for H_2O and values for D_2O all corrected for anharmonicity the observed ratio is 1.884.

This good agreement is encouraging enough to use H_2O and D_2O data to calculate the potential constants. Only three of the four frequencies $\omega_\pi{}^H$, $\omega_\delta{}^H$, $\omega_\pi{}^D$, $\omega_\delta{}^D$ need be used. It is most convenient to select three, calculate the fourth by (21) and use all four with invariants of (19)—that is the traces and determinant. If we put

[2] K. Freudenberg and R. Mecke, Zeits. f. Physik **81**, 465 (1933).

[3] L. Bonner, Phys. Rev. **46**, 458 (1934).

$m_2\lambda_i=\kappa_i$ the traces of $D^{(3)}(A_1)$ for the two molecules yield

$$z_+=\kappa_\pi{}^H+\frac{\kappa_\delta{}^H-\kappa_\pi{}^D}{\mu_H{}^2-\mu_D{}^2}-\kappa_\delta{}^D, \qquad (22)$$

$$y_-=\kappa_\pi{}^H+\kappa_\delta{}^H-\mu_H{}^2 z_+.$$

The determinant gives

$$w_-=\pm(z_+y_--\lambda_\pi\lambda_\delta(m_1m_2{}^2/M))^{\frac{1}{2}}. \qquad (23)$$

Force constants in $r\theta$ coordinates are more significant from a theoretical standpoint (yz coordinates were used above because of the simplicity of the equations); they can be calculated from the transformation

$$\begin{Vmatrix}\cos\alpha & \sin\alpha\\ -\sin\alpha & \cos\alpha\end{Vmatrix}\begin{Vmatrix}z_+ & w_-\\ w_- & y_-\end{Vmatrix}\begin{Vmatrix}\cos\alpha & -\sin\alpha\\ \sin\alpha & \cos\alpha\end{Vmatrix}=\begin{Vmatrix}\rho_+ & \varphi_+\\ \varphi_+ & \theta_+\end{Vmatrix}, \qquad (24)$$

where
$$\rho_+=v_{r_2r_2}+v_{r_2r_3},$$
$$\theta_+=v_{\theta_2\theta_2}+v_{\theta_2\theta_3}=2v_{\theta_2\theta_2} \quad \text{from (12)},$$
$$\varphi_+=v_{r_2\theta_2}+v_{r_2\theta_3}=2v_{r_2\theta_3} \quad \text{from (12)}. \qquad (25)$$

Only ρ_+ need be calculated by matrix multiplication, the trace and determinant of (24) give

$$\theta_+=z_++y_--\rho_+,\ \varphi_+{}^2=\rho_+\theta_+-(z_+y_--w_-{}^2). \qquad (26)$$

Actual values of these force constants were calculated using Bonner's values of the corrected frequencies $\omega_\sigma{}^H$, $\omega_\pi{}^H$, $\omega_\delta{}^H$ obtained from analysis of a large number of infrared bands. In the next paper the anharmonicities for D_2O are calculated and applied to the observed frequencies.[4] As only one of these need be chosen, $\omega_\delta{}^D$ was selected as $\omega_\pi{}^D$ was determined from the Raman spectrum about which there may be some doubt. In the Raman spectrum of H_2O the observed value of π vibration (uncorrected for anharmonicity) is 3654 in the Raman spectrum,[5] whereas the value calculated from infrared is 3604 cm^{-1}, a difference of 54 cm^{-1}. Assuming $\omega_\delta{}^H$, $\omega_\delta{}^D$, $\omega_\pi{}^H$ (infrared) formula (21) would be exactly satisfied by a π vibration (uncorrected for anharmonicity) of 2638 which differs from the observed Raman line 2666 cm^{-1} by 27.7 cm^{-1}. Allowing for an isotope effect the same discrepancy between the Raman and infrared frequencies seems to occur in D_2O as in H_2O.

From the values

$$\omega_\delta{}^H=3899.0\ \text{cm}^{-1},\quad \omega_\delta{}^D=1210.5\ \text{cm}^{-1},$$
$$\omega_\pi{}^H=3807.5\ \text{cm}^{-1},\quad (\omega_\pi{}^D=2745.6)\ \text{cm}^{-1},$$
$$\omega_\delta{}^H=1654.5\ \text{cm}^{-1},$$

the force constants are calculated to be (units of megadynes/cm)

$$z_+=0.3567,\quad \rho_+=0.8211,\quad v_{r_2r_2}=0.8269,$$
$$y_-=0.6169,\quad \theta_+=0.1526,\quad v_{r_2r_3}=-0.00585,$$
$$w_-=0.3114,\quad \varphi_+=-0.0469,\quad v_{\theta_2\theta_2}=0.07632,$$
$$\rho_-=0.8325,\quad v_{r_2\theta_3}=-0.02346.$$

For further calculation of intensities or anharmonicities the numerical value of the matrix $P(A_1)$ which diagonalizes $D^{(3)}(A_1)$ is wanted. Being orthogonal it is of the form

$$P(A_1)=\begin{Vmatrix}\cos\vartheta & \sin\vartheta\\ -\sin\vartheta & \cos\vartheta\end{Vmatrix} \qquad (27)$$

with ϑ given by the equation

$$\sin 2\vartheta=\frac{-2}{m_2}\left(\frac{m}{m_1}\right)^{\frac{1}{2}}\frac{w_-}{\lambda_\pi-\lambda_\delta}. \qquad (28)$$

The motion of the hydrogen atoms in the π vibration makes an angle $\tan^{-1}\mu^{-1}\tan\vartheta-\alpha$ with the bond direction, which is 17° 28′ for H_2O and 17° 17′ for D_2O.

The evaluation of the terms in the general quadratic expression form a nucleus for a collection of correct force constants—augmented with similar results from H_2S, H_2Se, methane, ethylene, etc., which should indicate the order of magnitude of similar constants, especially cross terms, to be used in the calculation of frequencies in molecules where the potential function cannot be obtained from theory or experiment. Of especial interest is the bending constant, which, in agreement with an empirical rule derived from linear molecules, is about 10 percent of the bonding constant: the high value of 17 percent $v_{r_2r_2}$ of H—H repulsion is in

[4] W. V. Norris, H. J. Unger, R. E. Holmquist, Phys. Rev. **49**, 272 (1936).
[5] D. F. Bender, Phys. Rev. **47**, 252 (1935), *et al.*

TABLE I. *The energy, $f(r)$, of OH bonding.*

MEGADYNES/CM		CURVATURE f''	SLOPE (PER CM) f'/r
i	Observed in OH molecule	0.7757	0
ii	Observed in H_2O, Eq. (31)	.8386	0.0109
iii	Predicted by Badger's rule	.800	—
iv	Predicted by (32)	—	0.0073
v	Predicted by Morse function for OH	.8252	0.0075
vi	Predicted by introduction of ionic terms in the Morse function	.8356	0.0070
vii	Predicted by introduction of ionic terms in the Morse function	.8306	.011
viii	Predicted by addition of ionic terms	.8386	.013

accordance with indications from other molecules. In water, at any rate, the valence and central models contribute equally to the molecular function.

The constants determined above are probably reliable, as they favorably withstand two tests. The frequencies of HDO can be calculated since both V and T are now known, but the presentation of this confirmation will have to be postponed since comparison with experiment also requires the determination of anharmonicity constants for HDO.

In the second test the actual constants are compared with those of a theoretically constructed molecule based on the S−P picture of directed valence. Since the constants differ somewhat from those estimated by Van Vleck and Cross[6] for such a model, it is interesting to see to what parameters in the energy functions the actual values correspond. In this each hydrogen is joined independently to the oxygen as it is in OH chiefly by the overlapping $f(r)$ of the orbital of the hydrogen $1s$ electron with one of the three p orbitals in oxygen which are oriented at right angles. The mutual effect of the hydrogen is $1s-1s$ repulsion $g(r_{12})$ increasing the angle. The stiffness of the angle $h(\alpha)$ is due to two important exchange integrals—the actual bonding A to one p orbital and exchange with the other two $\frac{1}{2}B$, formulated by Slater[7] as

$$h(\alpha)=3(A-B)\sin^2(\alpha/2-\pi/4). \qquad (29)$$

Lacking exact computation the potential function is estimated as a central force model of Morse functions of OH and H_2 with a valence force model using Slater's angular function,

$$v=f(r_1)+f(r_2)+g(r_{12})+h(\alpha). \qquad (30)$$

By (3)

$$\begin{aligned}
f''&=v_{r_2r_2}+\cos\alpha v_{r_2r_3}-\tfrac{1}{2}\sin 2\alpha\, v_{r_2\theta_3}\\
&=0.8386 \text{ megadynes/cm},\\
f'/r&=-\sin^2\alpha(-2v_{r_2r_3}+\tan\alpha\, v_{r_2\theta_2})\\
&=0.0109 \text{ megadynes/cm},\\
g''&=v_{r_2r_3}+\tfrac{1}{2}\cot\alpha\, v_{r_2\theta_3}\\
&=-0.0149 \text{ megadynes/cm},\\
g'/r&=\sin\alpha(-2v_{r_2r_3}+\tan\alpha\, v_{r_2\theta_2})\\
&=-0.0143 \text{ megadynes/cm},\\
h''/r&=v_{\theta_2\theta_2}-4v_{r_2r_3}-4\cot 2\alpha\, v_{r_2\theta_3}\\
&=0.0751 \text{ megadynes/cm},\\
h'/r^2&=-\sin 2\alpha(-2v_{r_2r_3}+\tan\alpha\, v_{r_2\theta_3})\\
&=0.0181 \text{ megadynes/cm},
\end{aligned} \qquad (31)$$

The fact that g'' and g'/r have the correct sign (showing hydrogen repulsion) alone is gratifying, since this is not so when frequencies uncorrected for anharmonicity are used. The value of the force constant f'' being almost that in OH substantiates the conception of directed valence bonding, but even the discrepancy is in good agreement with more detailed considerations. First, the increase of the constant with decrease in internuclear distance, $r_{OH}=0.964$, $r_{H_2O}=0.955$A, is in agreement with Badger's rule as shown in Table I (*iii*).

Were the bonding function the same in H_2O as OH, for such small displacements

$$f'_{H_2O}=f'_{OH}+\Delta r f''_{OH}, \qquad (32)$$

a relation not satisfied by the data (Table I, *iv*). The discrepancy is probably due to increased ionic character in the H_2O molecule, a phenomenon predicted by theory. A correction for a small increase in ionic character say x percent can be estimated[8] by multiplying the Morse function by $100+x$. A Morse function alone gives values, in agreement with (32), shown in the line *v* of Table I, while 1.5 percent ionic character raises f'' to the correct value but leaves f'/r still too low (*vi*). The change due to the introduction of small amounts of "ionic" wave functions affects the exponential factor in

[6] J. H. Van Vleck and P. Cross, J. Chem. Phys. **1**, 387 (1933).
[7] J. C. Slater, Phys. Rev. **38**, 1109 (1931).
[8] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

the Morse function rather than the dissociation energy, 1.5 percent ionic character giving in this case the correct values, *vii* of Table I.

Still a third way of calculating the change follows from the additivity of the differentials of terms in the potential energy. Pure ionic attraction would correspond to

$$V=e^2/r, \tag{33}$$

$$\frac{\partial V}{\partial r}=-\frac{0.230}{r^2}\,10^{-5}\text{ dynes}, \tag{34}$$

$$\frac{\partial^2 V}{\partial r^2}=\frac{0.46}{r^3}\text{ megadynes/cm}, \tag{35}$$

and 2.5 percent ionic character giving about the right correction to both constants (*viii*, Table I).

The hydrogen repulsion $g(r_{12})$ can be similarly estimated from the Morse function for H_2, for which the parameters are determined from the values $\omega_e=4371.9$ and $D_e=4.722$ ev. As shown by Van Vleck and Cross x percent ionic character in the energy of nonbonded atoms can be represented by a Morse function multiplied by a factor $x/100\times\frac{1}{2}(1-x/100)$. At the internuclear distance $2r\sin\alpha=1.512$A 20 percent ionic character gives the observed $g''=-0.0149$, and $g'/r=-0.0116$ whereas the observed g'/r is -0.0148.

The more detailed picture of the *angular* function (29) can be confirmed in two independent ways by the data: the agreement reveals the extent to which the data are self-consistent.

$$h''/r^2=6(A-B)/r^2\sin 2\alpha, \tag{36}$$

$$h'/r^2=-3(A-B)/r^2\cos 2\alpha, \tag{37}$$

giving for $(A-B)/r^2$ the values 2.96 and 3.26 ev/A, in agreement with the values of the exchange integrals calculated by Coolidge.[9] Using the value used in the computations, one has $(A-B)/r^2=2.9$. The actual calculation of Coolidge did not give the correct energy, probably due to lack of ionic terms. However, the above agreement is not fortuitous since ionic terms would not contribute to the angular (orientation) part, $h(\alpha)$, unless they were large.

Conclusions

The hydrogen isotope does not change the potential function of H_2O to within the accuracy of measurement of the vibrational levels. If this is assumed the angle can be calculated as 107° 22′, agreeing with the value obtained from rotational analysis, and all force constants in a general quadratic potential function can be determined, showing that valence and central force constants are equally important, and that cross terms are not negligible with respect to the lowest frequency. These constants are of the magnitude predicted by the S−P picture of molecular structure in regard to the OH bonding, H−H repulsion and stiffness of orientation.

These computations were achieved by a matrix method of handling changes of coordinates, of general application, leading to accurate formulae for studying the isotope effect, identifying bands and determining the angle. As shown in the following paper the method is especially useful in calculating the perturbation of the energy levels due to higher and cross terms in the potential functions, and the effect of the isotope thereon.

[9] A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

Anharmonicity Constants of the Potential Function of the Water Molecule

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The vibrational energy levels of a polyatomic molecule with quartic terms in the potential function are determined by matrix mechanics, and the change on substitution of an isotope formulated. Applied to H_2O and D_2O, frequencies at the zero point are obtained that satisfy invariants calculated for harmonic motion.

BONNER[1] derived by a wave-mechanical treatment the first-order perturbations of the energy levels of three coupled oscillators with quartic terms in the potential function, and estimated the isotope effect in D_2O. In the previous calculations[2] the theoretically interesting cross terms are exceedingly sensitive to changes in the frequencies, so that it was essential to determine the anharmonicity constants for D_2O with certainty.

For use with vibrational levels of low quantum numbers quite probably the energy of an N atomic molecule can be expressed as a Taylor's expansion in $3N$ Cartesian coordinates, x_i

$$V=\sum v_{ij}x_ix_j+v_{ijk}x_ix_jx_k + \cdots v_{t_1t_2\ldots t_p}x_{t_1}x_{t_2}\ldots x_{t_p} \quad (1)$$
$$=\sum_p\sum_i v_{t_1t_2\ldots t_p}x_{t_1}x_{t_2}\ldots x_{t_p}, \quad i_p=1, 2, \cdots 3N,$$

$p=2$ to the number of terms to be taken in the Taylor's expansion.

$$v_{t_1t_2\ldots t_p}=\frac{1}{p!}\frac{\partial^p V}{\partial x_{t_1}\partial x_{t_2}\cdots\partial x_{i_p}}.$$

If a transformation to coordinates ξ_i be made by

$$x_i=\sum_j q_{ij}\xi_j, \quad Q=\|q_{ij}\|, \quad (2)$$

then
$$V=\sum_p\sum_i \lambda_{t_1t_2\ldots t_p}\xi_{t_1}\xi_{t_2}\cdots\xi_{t_p}, \quad (3)$$

where
$$\lambda_{t_1t_2\ldots t_p}=\sum_\mu v_{\mu_1\mu_2\ldots\mu_p}q_{t_1\mu_1}q_{t_2\mu_2}\cdots q_{t_p\mu_p}. \quad (4)$$

By the previously described normal coordinate treatment the matrix Q is chosen so that if $V=V^{(2)}=\|v_{ij}\|$

$$\Lambda^{(2)}=Q'VQ=\Lambda \quad \text{diagonal} \quad \lambda_{ij}=\lambda_i\delta_{ij}; \lambda_i=\omega_i^2.$$

In the $\Lambda^{(p)}$'s the range of the indices is now only $3N-5$ or 6 since rotations and translations occur with zero force constants.

Quadratic cross terms being absent, quantum theory can be simply introduced by matrix mechanics. If $\mathbf{P}_i$ and $\mathbf{Q}_i$ be the well-known infinite matrices which satisfy the commutation rules and diagonalize the Hamiltonian for simple harmonic motion in the ith normal coordinate (whence the masses are unity)

$$\tfrac{1}{2}(\mathbf{P}_i^2+\lambda_i\mathbf{Q}_i^2)=\mathbf{W}_i^\circ \quad (5)$$

take as matrices $\mathbf{P}$ and $\mathbf{Q}$ for the system

$$\mathbf{P}=\mathbf{P}_1\times\mathbf{P}_2\times\mathbf{P}_3\times\cdots, \quad \mathbf{Q}=\mathbf{Q}_1\times\mathbf{Q}_2\times\mathbf{Q}_3\times\cdots, \quad (6)$$

and define

$$\mathbf{W}^\circ=\mathbf{W}_1^\circ\times\mathbf{I}\times\mathbf{I}\times\cdots+\mathbf{I}\times\mathbf{W}_2^\circ\times\mathbf{I}\times\cdots +\mathbf{I}\times\mathbf{I}\times\mathbf{W}_3^\circ\times\cdots. \quad (7)$$

Since the indices can be permuted without changing the value we can write $\lambda_{1_1\ldots1_i2_1\ldots2_j3_1\ldots3_k\ldots}$ for a λ with i indices equal to the cardinal number 1, j indices equal to the cardinal 2, k of 3, etc. Then the Hamiltonian[3] of the whole system is

$$H=\mathbf{W}^\circ+\tfrac{1}{2}\{\sum_{ijk}\lambda_{1_i\ldots1_i2_1\ldots2_j3_1\ldots3_k\ldots}\mathbf{Q}_1^i \times\mathbf{Q}_2^j\times\mathbf{Q}_3^k\times\cdots\}. \quad (8)$$

* National Research Fellow in Chemistry.
[1] L. Bonner, Phys. Rev. **46**, 458 (1934).
[2] "The Potential Function of the Water Molecule," J. Chem. Phys. **5**, 405 (1937).

[3] Professor E. B. Wilson has very kindly discussed the relation of this to the precise Hamiltonian given by E. B. Wilson and T. B. Howard, J. Chem. Phys. **4**, 236 (1936), Eq. (33). Our simplified Hamiltonian is only valid as long as rotations can be regarded as *linear* combinations of Cartesian displacements and represented by a column in the matrix Q (Eq. (2)), which is of order $3N$, not $3N-6$: that is, it is valid for low quantum numbers, to which region its application is restricted.

Converting to the wave number energy scale, putting $B_i=(h/(8\pi^2\omega_i))^{\frac{1}{2}}$ and

$$c_{ijk\ldots}=\lambda_{ijk\ldots}/2hcB_iB_jB_k\cdots \tag{9}$$

the energy matrix can be diagonalized by perturbation theory if the potential constants $c_{i_1i_2\ldots i_p}$, $p\geq 3$, are small compared with ω_i (i.e. with the $c_{i_1i_2}$'s). First-order corrections are the diagonal elements which come only from the matrices $\mathbf{Q}_1{}^i\times\mathbf{Q}_2{}^j\times\mathbf{Q}_3{}^k\times\cdots$ in which no i, j, k is odd.

$$\begin{aligned}E_{n_1n_2n_3\ldots}=&\sum_i\omega_{n_i}(n_i+\tfrac{1}{2})+3(2n_1{}^2+2n_1+1)c_{1111}\\&+3(2n_2{}^2+2n_2+1)c_{2222}+\cdots\\&+(2n_1+1)(2n_2+1)c_{1122}\\&+(2n_1+1)(2n_3+1)c_{1133}\cdots.\end{aligned} \tag{10}$$

Collecting terms,

$$E_{n_1n_2n_3\ldots}=X_0+\sum_iX_in_i+\sum_iX_{ii}n_i{}^2+\sum_{i>j}X_{ij}n_in_j \tag{11}$$

with

$$\begin{aligned}X_0&=\sum_i\omega_i/2+3\sum_ic_{iiii},\\X_i&=\omega_i+6c_{iiii}+2\sum_jc_{iijj},\\X_{ii}&=6c_{iiii},\\X_{ij}&=4c_{iijj}.\end{aligned} \tag{12}$$

To calculate force constants of the molecule we need the frequencies at the bottom of the potential bowl, which from (11) are

$$\omega_i=X_i-X_{ii}-\tfrac{1}{2}\sum_jX_{ij}. \tag{13}$$

Eqs. (12) were found to determine the change in the X's when a different transformation to normal coordinates is made, for, although in the isotope effect V is assumed to be the same, Q and hence the λ_{ijk}'s and c's are different.

If Q^H is the transformation for the molecule with one set of masses

$$Q^{H\prime}VQ^H=\Lambda^H \text{ diag.} \tag{14}$$

and Q^D is the one for another set of masses

$$Q^{D\prime}VQ^D=\Lambda^D \text{ diag.} \tag{15}$$

and Z is the product $Q^{H-1}Q^D$ which can be determined accurately enough by successive approximations to the zero-point frequencies, then

$$\begin{aligned}\lambda^{(D)}{}_{i_1i_2\ldots i_p}&=\sum_\mu q^{(D)}{}_{i_1\mu_1}q^{(D)}{}_{i_2\mu_2}\cdots q^{(D)}{}_{i_p\mu_p}v_{\mu_1\mu_2\ldots\mu_p}\\&=\sum_{\nu,\,\mu}z_{\nu_1i_1}z_{i_2i_2}\cdots z_{\nu_pi_p}q^{(H)}{}_{\nu_1\mu_1}q^{(H)}{}_{\nu_2\mu_2}\\&\qquad\cdots q^{(H)}{}_{\nu_p\mu_p}v_{\mu_1\mu_2\ldots\mu_p}\qquad(16)\\&=\sum_\nu z_{\nu_1i_1}z_{\nu_2i_2}\cdots z_{\nu_pi_p}\lambda^{(H)}{}_{\nu_1\nu_2\ldots\nu_p}.\qquad(17)\end{aligned}$$

The assumption was that the v_{ijk}'s remained unchanged, not the λ_{ijk}'s (linear combinations of the v_{ijk}'s with coefficients containing the masses), but Z and (17) had to be formulated because the v's are not measurable, only the λ_{ijk}'s of the one molecule, (9) and (11). By the latter, however, only certain λ_{ijk}'s are measured —not all of those that occur on the right of (17). The problem thus cannot be solved rigorously, the anharmonicity constants of the isotope contain more constants (λ_{ijk}) because the λ_{ijk}'s are linear combinations of several v_{ijk}'s. The difficulty is easily overcome. In the case of triatomic molecules with hydrogen the matrix is very nearly diagonal (see 25). Because the matrices[4] $D^{(r_i)(3)}$ are of the form $L^{(r_i)}V^{(r_i)}L^{(r_i)}$, Z is also made up of main diagonal blocks, one for each representation, so that outside of these the nondiagonal elements are exactly zero.

If, for a first-order calculation Z is replaced by a diagonal $\|f_i{}^{\frac{1}{2}}\|$, $f_i=\lambda_i{}^{(D)}/\lambda_i{}^{(H)}$ with the f's considered as parameters whose value can be made as accurate as desired by successive approximations, the summation (17) reduces to

$$\lambda^{(D)}{}_{i_1i_2\ldots i_p}=f_{i_1}{}^{\frac{1}{2}}f_{i_2}{}^{\frac{1}{2}}\cdots f_{i_p}{}^{\frac{1}{2}}\lambda^{(H)}{}_{i_1i_2\ldots i_p}. \tag{18}$$

Substitution in (12) leads to

$$X_i{}^D=f_i{}^{\frac{1}{2}}\omega_i{}^H+6f_ic^H{}_{iiii}+2f_i{}^{\frac{1}{2}}\sum_jf_j{}^{\frac{1}{2}}c^H{}_{iijj}, \tag{19}$$

$$X_{ii}{}^D=f_iX_{ii}{}^H, \tag{20}$$

$$X_{ij}{}^D=f_i{}^{\frac{1}{2}}f_j{}^{\frac{1}{2}}X_{ij}{}^H. \tag{21}$$

Eq. (20) is exact for the σ vibration, since $Z(B_2)$ is of first order and equals $f_\sigma{}^{\frac{1}{2}}$.

[4] See previous paper, Eq. (12).

Application to Water

Preliminary calculation with frequencies uncorrected for anharmonicity shows that Z can indeed be replaced without great error by the diagonal matrix $\|f_i^{(1)\frac{1}{2}}\|$, $f_i^{(1)}$ being the ratio of the observed frequencies, in which case the unknown anharmonicity constants of D_2O are given by the formulae of the last paragraph. With the latter first-order approximations to the X's of D_2O the observed frequencies are corrected for anharmonicity giving $\omega_\sigma^D=2865.4$, $\omega_\pi^D=2764.7$, $\omega_\delta^D=1209.7$. The latter are now used to get better values for f_i and hence to get improved X^D's. The second approximation to $f_\sigma^{\frac{1}{2}}$, 1.3632, already agrees with the value

$$f_\sigma^{\frac{1}{2}}=\left(\frac{2\sin^2\alpha}{m_1}+\frac{1}{m_2{}^H}\right)^{\frac{1}{2}}\Big/\left(\frac{2\sin^2\alpha}{m_1}+\frac{1}{m_2{}^D}\right)^{\frac{1}{2}}=1.3647 \quad (22)$$

derived in the previous paper. The values of f_π and f_δ are not determined independently of the frequencies as is f_σ because they belong to frequencies in the same representation.

Another way of testing the theory is actually to calculate the position of the fundamental ν_σ^D and compare with the wave-length observed:

$$\begin{aligned}\nu_\sigma^D&=\omega_\sigma^D+2X_{\sigma\sigma}{}^D+\tfrac{1}{2}(X_{\sigma\pi}{}^D+X_{\delta\delta}{}^D)\\&=f_\sigma^{\frac{1}{2}}\omega_\sigma+2f_\sigma X_{\sigma\sigma}{}^H\\&\quad+\tfrac{1}{2}f_\sigma^{\frac{1}{2}}(f_\pi^{\frac{1}{2}}X_{\sigma\pi}{}^H+f_\delta^{\frac{1}{2}}X_{\sigma\delta}{}^H)\end{aligned} \quad (23)$$

with $f_\sigma=$ the function of masses and angles (22). Since f_π and f_δ only multiply correction terms, a rough approximation based only on a simple model will suffice. The calculated value is $\nu_\sigma^D=2781$ cm^{-1}, the observed 2784 cm^{-1}.

Symmetrical Representation

By means of (19–21) and successive approximations, the observed bands[5] at $\nu_\pi^D=2666$ cm^{-1} and $\nu_\delta^D=1179$ cm^{-1} yield corrected frequencies $\omega_\pi^D=2773.3$ and $\omega_\delta^D=1210.5$. These can be tested by the formula

$$\omega_\pi^D\omega_\delta^D=\frac{m_2{}^H}{m_2{}^D}\left(\frac{m^D}{m^H}\right)^{\frac{1}{2}}\omega_\pi^H\omega_\delta^D=3.324. \quad (24)$$

From experimental data this is 3.357.

The constants for the energy formula for D_2O are

$$\begin{aligned}&\omega_\delta^D=2857.0, \quad X_{\sigma\sigma}{}^D=-21.2, \quad X_{\sigma\pi}{}^D=-56.5,\\&\omega_\pi^D=2773.5, \quad X_{\pi\pi}{}^D=-37.0, \quad X_{\sigma\delta}{}^D=-11.3,\\&\omega_\delta^D=1210.5, \quad X_{\delta\delta}{}^D=-10.4, \quad X_{\pi\delta}{}^D=-10.1.\end{aligned}$$

Better Approximation

So far we have taken Z to be diagonal. Now we can investigate changes when nondiagonal elements are taken into account. With frequencies estimated as above Z is

$$Z=\begin{Vmatrix}0.7166 & 0.0646\\0.0123 & 0.7374\end{Vmatrix}. \quad (25)$$

These values can be improved by successive approximations, but the ratio z_{ij}/z_{ii} remains small enough for z_{ij}^2 to be entirely neglected relative to the main diagonal elements, and the summation (17) reduces to fewer terms. The important constants are

$$\begin{aligned}\lambda^D{}_{iiii}&=z_{ii}{}^4\lambda^H{}_{iiii}+\sum_{j\neq i}z_{ii}{}^3z_{ji}\lambda^H{}_{iiij},\\\lambda^D{}_{iijj}&=z_{ii}{}^2z_{jj}{}^2\lambda^H{}_{iijj}+\sum_{k\neq j}z_{ii}{}^2z_{jj}z_{kj}\lambda^H{}_{iijk}\\&\quad+\sum_{k\neq i}z_{ij}{}^2z_{ij}z_{ki}\lambda^H{}_{jjki},\end{aligned} \quad (26)$$

so that

$$\begin{aligned}X_{ii}{}^D&=f_i{}^{-1}z_{ii}{}^4X_{ii}{}^H+f_i{}^{-1}z_{ii}{}^3\sum_j z_{ji}[6c^H{}_{iiij}],\\X_{ij}{}^D&=f_i{}^{\frac{1}{2}}f_j{}^{\frac{1}{2}}z_{ii}{}^2z_{jj}{}^2X_{ij}{}^H\\&\quad+f_i{}^{\frac{1}{2}}f_j{}^{\frac{1}{2}}\{z_{ii}{}^2z_{jj}\sum_{k\neq j}z_{kj}[6c^H{}_{iijk}]+z_{ii}z_{jj}{}^2\sum_{k\neq j}z_{ki}[6c^H{}_{jjik}]\}.\end{aligned}$$

The constants $c^H{}_{iiij}$, $c^H{}_{iijk}\sim\lambda^H{}_{iiij}$, $\lambda^H{}_{iijk}$ occur, which cannot be determined from one molecule. They could be derived by experimental determination of the $X_{ij}{}^D$'s in the isotopic molecule. However, they enter with relatively small coefficients and no doubt can be estimated as being equal in magnitude to the λ_{iijj}'s (which are all nearly equal). For water (26) corresponds to

$$\begin{aligned}X_{\pi\pi}{}^D&=0.500X_{\pi\pi}{}^H+0.00857[6c^H{}_{\pi\pi\pi\delta}],\\X_{\delta\delta}{}^D&=0.553X_{\delta\delta}{}^H+0.0484[6c^H{}_{\delta\delta\pi\pi}],\end{aligned}$$

Substitution gives an increase of 2 cm^{-1} in $X_{\pi\pi}{}^D$ above that calculated by a diagonal Z, and a decrease of 1 cm^{-1} in $X_{\delta\delta}{}^D$.

Although nondiagonal elements are not entirely negligible, the diagonal elements of Z have changed enough from the f_i's to counteract the effect.

[5] W. V. Norris, H. J. Unger, R. E. Holmquist, Phys. Rev. 49, 272 (1936).

The Energy States of Crystalline $Pr_2(SO_4)_3 \cdot 8H_2O$

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The absorption spectra of $Pr_2(SO_4)_3 \cdot 8H_2O$ were photographed when the salt was at 20°K, 78°K, 105°K, 169°K, 200°K and 300°K. At least three low lying excited levels were found to exist beside the basic one and they appear to be located at 110, 235 and 500 cm^{-1} above the basic state. They are therefore in fair agreement with the calculations of Penney and Schlapp and with the field constant D for the rare earth sulphates which was determined spectroscopically for Nd and Er. A very strong coupling of vibrational states with the highly excited energy states seems to occur as the absorption bands consist of hundreds of closely spaced lines.

PENNY and Schlapp[3] by means of group theory and wave mechanics have calculated how the magnetic susceptibilities of crystalline $Pr_2(SO_4)_3 \cdot 8H_2O$ and $Nd_2(SO_4)_3 \cdot 8H_2O$ vary with the temperature. They made the simplifying assumptions that Russell Saunders coupling would hold for the basic state and that the crystalline field was mainly due to the octahedron of oxygen atoms which surrounds the rare earth ion and would accordingly be predominantly cubic.[4] In deriving their expression for the magnetic susceptibility they necessarily calculated the splitting of the basic state in the fields they assumed, and in the case of Nd their assumptions must have been justified for the levels were found spectroscopically in the positions demanded by theory.[5] Further, using the constants determined from Nd similar calculations for Er predicted levels in the positions where they had been previously found.[6] In the cases of Sm and Dy the observed levels were not in the positions predicted by simple theory. Such deviations would be expected, however, if the contention of one of us[7] that an additional low lying electronic level occurs in these salts is correct. A study of Pr, therefore, should be particularly valuable in extending the application of these methods to solids. We hoped also at the beginning of this work to be able to prove or disprove the contention of Van Vleck[8] and others that all observed transitions are of the so called forbidden type $4f^n - 4f^n$. Since there are only two $4f$ electrons in Pr the number of possible excited states is extremely limited and knowing the fields present from the basic state, it should be easy to calculate the splitting patterns of these excited states. Unfortunately we found that the excited states were strongly coupled with vibrational frequencies so that hundreds of lines appeared, and we have not as yet succeeded in interpreting them.

Experimental Part

Two different Pr salts were used in this investigation. The one which was used for most of the work was from the supply of the Cornell chemistry department and was of very high purity, for even with very thick conglomerates no absorption lines of other rare earths were observed. The other belonged to the chemistry department of the University of California and contained a small amount of Nd, for the stronger lines of that element were clearly evident in a thick conglomerate. This salt was used to obtain the absorption spectra of $Pr_2(SO_4)_3 \cdot 8H_2O$ at 20°K. Nutting, Meehan and Kraus of the University of California very generously made these photographs and sent us the plates for measurement. The single crystal used was 1.6 mm thick and the conglomerate was about 4 mm

[1] Baker Research Fellow.
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[2a] On leave of absence from University of Kentucky.
[3] Penney and Schlapp, Phys. Rev. **41**, 194 (1932).
[4] Penney and Schlapp expressed the potential energy as a power series. As the field was cubic the first terms which differed from zero were $V = D(x^4+y^4+z^4)+\cdots$. They neglected all terms higher than the fourth power.
[5] Spedding, Hamlin and Nutting, J. Chem. Phys. **5**, 191 (1937).
[6] Spedding, J. Chem. Phys. **5**, 316 (1937).
[7] Spedding and Bear, Phys. Rev. **46**, 975 (1934).
[8] Van Vleck, J. Phys. Chem. Jan. (1937).

TABLE I.* *Frequencies of absorption lines of solid $Pr_2(SO_4)_3 \cdot 8H_2O$.*

Angstroms	20°K Single Crystal Wave No.	Int.	20°K Conglomerate Wave No.	Int.	78°K Single Crystal Wave No.	Int.	78°K Conglomerate Wave No.	Int.	
6049.4					16526	0*d*	16519	1*vd*	*hx*
42.8					44		43		*hy*
33.3					70	1*d*	69	4*vd*	*hx*
27.1					87		87		*hy*
13.0			16626	0*d*			16625		
10.5	16633.0	4*s*	32.1	10*d*	16632	10*d*		10*vd*	*hx*
07.6			41	0*d*					
05			44	0*d*	48		50		
02	56	0*d*	55	2*d*					
5994.3	78	0*d*	79	0*d*	81	7*vd*	80	10*vd*	
92.1	84.0	8*s*	83	10*d*					
91.6			85.5						
90.5	88.4		88						
89.7	90.6	2*d*	90	3*d*					
89.0			92.6	1*d*					
88.2			95	0					*hx*
86.8	98.7	0*d*	98	2*d*	16700		16700		
83.7	16707.5	0*d*							
81.3	14	0*d*							
78.5	22.0	1*d*	16721.5	2*d*					
77.0	26	2*d*	26	5*d*	25	continuum	25	continuum	
75.6	30	0*d*	30.5	1*d*			27		
74.7	32.5	1*vd*	33.5	2*vd*					
73.1	37	1*vd*	35.5	2*vd*				2*d*	
72.0	40.3	1*d*							
71.2	42.3	10*s*	42	10*d*					
70.2	45.1		47.1						
68.5	49.9		52				57		
66.4	56	0*d*							
64.9	60	2*d*	60.5	5*d*					
63.3	64.7	1*d*	65.1	2*d*	65				
61.5	69.7	3*d*	69.4	6*d*					
60.2	73.2	1*d*							
58.5	78.1	4*s*	78	continuum					
57.7	80.2								
57.2	81.9					8*vd*			
55.7	85.9	6*s*							
54.0	90.7	6*d*							
53.2	93.1								
49.2	16804.4	8*d*							
46.3	12.6	10*d*							
46.2	12.9				16812				
44.7	17.1	2*d*							
42.8	22.4	7*d*							
40.8	28.0	4*d*							
38.1	35.8	5*d*							
35.9	42	continuum			42	8*vd*			
35.5	43.4	8*d*							
24.6					74				
18.0					93	4*vd*			
13.1					16907				
01.6	16940				40				
01.2	40.9	1*d*							
5898.5	48.8	2*d*							
95.3	58	10*d*							
92.7	65.4				66	2*d*			
90.1	73				78				
89.6	74.5	*vd*							
89.0	76.2	10*d*							
83.3	92.6	8*d*							
82.1	96								
73.5	17021	1*d*			17019	2*vd*			
70.7	29	3*vd*							
69.7	32	1*d*			38				
67.6	38	3*vd*			40	1*vd*			
65.2	45				52				
63.8	49								

TABLE I—(*Continued.*)

Angstroms	20°K Single Crystal Wave No.	Int.	20°K Conglomerate Wave No.	Int.	78°K Single Crystal Wave No.	Int.	78°K Conglomerate Wave No.	Int.	
5859.7	61	*vd*			60				
57.2	68.4	8*vd*							
55.6	73					2*vd*			
52.5	82	*vd*							
51.1	86	5*vd*							
49.4	91				99				
47.7	96	*vd*							
46.7	99	2*vd*							
44.6	17105	2*vd*							
40.5	17	*vd*							
38.8	22	*vd*							
38.1	24	3*d*							
36.1	30	3*d*	17130		17128				
34.1	35.7	10*s*	35.6	1*d*		5*vd*			
29.6	49	*vd*	42.3	1*d*					
27.6	55	1*d*			53				
25.5	61	1*d*							
			60						
21.5	73	*vd*			77		17174		
13.4	97	8*vd*	98			8*vd*			0*vd*
10.6	17205			10*vd*					
08.5	11.4	6*s*			17210				
05.1	21.5						17218		
04.3	23.8	6*d*							
00.2	36		17236				42		
			52	0*d*	45				
5793.6	55.5	0*d*							
91.2	62.7		62			0*vd*	63		
90.6	64.5	10*s*	65.8	10*s*			67.3		6*vd*
89.8	66.9		69				71		
87.0	75.4	1*d*			74				
83.7	85.3	0*vd*	85	0*d*					
78.1	17302		17303				17301		
76.9	05.5	2*d*	06	3*d*					1*vd*
75.7	09		09				17		
73.1									
70.4	25								
68.1	32	0*vd*	29	0*d*					
66.1	38								
62.4	49		50		17349	0*d*	50		
61.4	52	3*vd*	52	4*d*					1*d*
59.8	57		56				55		
57.5	63.7	0*d*					61		
53.1	77	0*d*							
51.5	83		84				86		
49.7	87.5	4*d*	87.7	4*d*			90		2*d*
48.5	91		91				95		
43.2							17407		0*vd*
40.2							16		
35.3	17431	0*vd*	17434	0			28		0*vd*
							37		
18.6	82		83				84		
17.3	86	5*d*	86.5	6*d*			87.5		5*vd*
16.9	87		89				92		
4890.5							20442		
89.6							46		0*d*
88.6							50		
81.7							79		
79.1							90		3*d*
76.4							20501		
68.8					20533		28		
67.9					37		37		10*vd* *hy*
66.0						2*vd*	45		
65.0					49		51		2*vd* *hy*
62.7							59		2*vd* *hx*
60.8							67		3*vd*
60.1							70		

continuum

continuum

TABLE I—(*Continued.*)

Angstroms	20°K Single Crystal Wave No.	Int.	20°K Conglomerate Wave No.	Int.	78°K Single Crystal Wave No.	Int.	78°K Conglomerate Wave No.	Int.	
4858.0							79		
57.0							83	1*d*	*hy*
56.1							87		*hx*
54.7							93		
52.3					20603		20604		
51.4					07	4*vd*	07	8*vd*	*hx*
49.5					15		13		
45.7							31		
43.3					41.2	1*d*			
39.9							56		
39.0			20659.6	1*d*	61	*s*	62	10*vd*	
37.6	20665.7		65		66	8*d*			
37.3		4*s*	66.7	10*s*					
36.4	70.7		71.6						
35.6			74		76	8*d*			*hx*
33.8			81.8	2*d*	81	*s*			
32.8			86	1*d*					
31.9			90	3*d*					
30.6	95.6	1*s*	95.5	6*s*					
28.4	20705.0	1*s*	20706.2	2*d*	20706	*s*			
27.1	10.6	*s*	11	*s*	12	10*d*			
25.8	16.3	6*d*							
24.4			22.3	8*d*					
23.0	28.3	8*d*							
22.0	32.4	*s*	34.5	*s*	33	8*d*			
20.8	37.6	1*d*	38	0*d*	39	*d*			
19.3	44.2	1*d*	45	0*d*	43.3	0*d*			
16.3	57	0*d*	57.0	2*s*					
15.4	60.7	2*d*	61.5	4*d*	61.5	0*d*			
12.8			72				20770		
12.5	73.5	3*d*	74.2	6*d*	75	1*d*	75.3	1*d*	
11.3			78.5		79				
09.9	84.5	2*d*	84.2	4*d*			84.4	1*d*	
08.7	89.4	1*d*	89						
08.4			91.2	2*d*	92		92		
07.7	94.1	2*d*	95.7	4*d*		2*d*		8*d*	
06.3	20800.1	2*s*	20801.3	3*d*	20802.4		99.5		
05.7			03				20805		
04.7	07.2	1*s*	05	3*d*					
04.2			09.5						
02.6	16.1	5*s*	16.6	6*s*			16		
02.2							18	3*d*	
01.4	21.6	5*s*	23.0	6*s*	22.6	1*d*			
00.8					24		25.5	5*d*	
4799.6	29.1	3*d*	30.0	3*s*			30		
97.8	37.1	3*d*	38.2	3*d*			40	0*d*	
96.1	44.5	2*s*	46	3*vd*			46		
94.5	51.5	6*d*	51		52				
94.1			53	8*d*		1*d*		7*d*	
93.4	56.1	2*d*	58	8*d*	58		56.5		
92.1			62				62		
90.5	68.6	0*s*	70.9	2*s*					
88.4			78						
87.0	84.1	1*d*	82	3*d*			83	1*d*	
86.6			86						
85.2							92		
85.0	93	3*d*	94	5*s*	92	1*d*	95.0	3*d*	
83.3	20900	0*d*	20900	0*d*			98.5		
							20906		
81.1	10.0	2*d*	10.7	4*s*	20910.1	1*d*	10.8	3*d*	
78.8			19.7	1*d*			16		
76.9			28.2	1*d*					
75.3			35.0	1*d*					
73.4			43.5	1*d*					
71.7			51				53		
70.6			55.7	2*vd*				1*d*	
69.9			59						
69.2			62		61.5	0*vd*	63		
68.5	65	0*d*	68.5	1*vd*					
67.4			70				70	0*d*	

continuum

TABLE I—(*Continued.*)

Angstroms	20°K Single Crystal Wave No.	Int.	20°K Conglomerate Wave No.	Int.	78°K Single Crystal Wave No.	Int.	78°K Conglomerate Wave No.	Int.	
4764.6			82.3	0*d*					
							94.6	0*d*	
60.6			21000				21000		
60.1	21002	3*d*	03	6*d*			05	3*d*	
58.7			08	4*d*	21007.5	1*d*			
58.1			11				12		
56.9			16						
56.3			19	5*d*			21		
55.6	22	1*d*	24	4*d*	24	0*d*		1*d*	
54.2			28				28		
52.2	37	0*d*	36	1*d*					
50.6			44	0*d*	46		45.5		*hx*
47.9			56			1*vd*		4*d*	
47.2	59	2*d*	58	5*d*			59		
46.8			61		68		65		
44.2	72.5	0*s*	71.6	0*d*	76	0*d*			
42.5			80	3*d*			81	1*d*	
41.4	85.1	0*s*	85				86		
39.7			92.6	1*d*			93	0*d*	
38.2			99.0	0*d*			98		
36.9	21105	1*s*	21105.4	2*s*	21106		21105		*hx*
35.8	09.7	4*s*	08.4					8*vd*	
35.6			10.6	10*s*	12	6*d*	10		*hx*
35.1			13.1						
33.2			21.3	1*d*	18		21		
31.0			31.2	0*d*					
29.8					36.7	0*d*			
29.0			40.0	2*d*					
28.4	43	1*s*	44.4	2*d*					
26.9	49.5	1*s*	49.3	1*d*			48		
26.0	53.6	*s*	53		52.6	*s*			
25.3	56.9	6	55.4	10*d*					
24.0	62.6	8				8			
23.4	65.3	*s*	64.8	10*d*					
22.8	68.1	1*s*	69.5	2*d*	67.3	*s*			
			71						
21.4	74	0*d*	75	1*d*	76	*s*			
19.8	81.5		79.8		80.7	8*d*			
19.3	83.9	8*s*	83.8	8*vs*					
18.7	86.5		89.2						
17.6	91.2	0*s*			90.4	9*d*			*hx*
16.3	97.0	0*s*	97.7	2*d*	21200				
13.6	21209.2	1*s*	21210.6	3*d*					
12.1	16.6	2*s*	17.5	5*d*					
11.0	21.0	2*s*	21.4	5*d*					
09.7	26.8	1*s*	25.6	3*d*	27	*vd*			
08.8			31						
08.6	31.6	1*s*	32	8*d*	32	6*d*			
07.5	36.8	5*s*							
06.8	40.0	1*s*			42	5*d*			
05.7	45.1	2*s*	44	*vd*	46	*vd*			
08.9	52.8	4*s*	51.7	8*d*					
03.4			55.4		55				
02.5	59.2	6*s*	57	8*d*	57.6	6*d*			
01.3	64.8	1*s*	64		63.5	5*d*			
01.2			65		65	*vd*			
00.2	69.7	1*s*							
4698.5	77.5	0*s*							
96.7	85.5	*s*			86	4*vd*			
95.9	89.0	5*s*			91				
94.1	97.3	4*s*							
93.2	21301.6	4*s*							
92.8	03.4	*s*							
92.2	05.9	*s*			21310	*vd*			
	14.0	7			13	8*vd*			
90.4	18.5	*s*			17	*vd*			
88.0	25.1	0*s*							

continuum

continuum

TABLE I—(*Continued.*)

Angstroms	20°K Single Crystal Wave No.	Int.	20°K Conglomerate Wave No.	Int.	78°K Single Crystal Wave No.	Int.	78°K Conglomerate Wave No.	Int.
4686.9	30.3	4*s*			30			
85.2	37.7	4*d*			35			
84.3					42	1*vd*		
82.8	48.9	2*d*			46			
80.0	61.6	1*d*			61	*vd*		
79.7	63				70	1*vd*		
73.3					92	3*vd*		
67.9					21417	1*vd*		
66.4					24	*vd*		
58.5					60	2*vd*		
53.5					83			
47.9					21509	2*vd*		
46.8					14			
42.9					32	2*vd*		
42.3					35			
34.8	21570				70			
34.0	73.8	1*d*						
28.6	99	*vd*			83	0*vd*		
26.7	21607.7	2*d*			21608.3			
24.7					17	2*vd*		
23.2	24	2*d*			20			
22.1					29			
18.3	47	2*d*			44	1*d*		
16.6	55	*vd*			53	2*vd*		
13.4	70	*vd*			70	1*vd*		
11.0	81	6*d*						
08.9	91							
04.5	21712.0	2*d*						
00.6	30.4	2*d*						
4594.7	58.2	2*d*						
90.0	80.5	*vd*						
89.0	85	2*d*						
85.2	21803	1*d*						
81.3	21.5	0*d*						
77.5	40	0*d*						
74.3	55	1*d*						
73.5	59	*vd*						
69.1	80	1*d*						
64.7	21901	1*d*						
62.6					21911			
59.5	26.2	5*s*			22	0*vd*		
56.8	39	3*d*			43			
47.3					85			
45.5	93.5				90.5	1*vd*		
41.7	22012	8*d*			22016	1*vd*		
38.9	25.5				29			
31.0	64	0*d*						
27.6	80.5	0*d*						
25.0	93	1*d*						
24.2	97							
20.2	22116.5	1*d*						
14.0	47							
13.2	51	2*d*						
12.9	52.4							
08.5	74	1*d*			22175.2	1*d*		
06.8					82.5			
05.3	90	1*vd*			91	1*vd*		
03.6					98			
03.2	22200	1*vd*						
00.8	12	1*vd*						
4497.8	27				22227			
97.1	30.4	8*d*				4*vd*		
96.4	34				36			
94.5	43				44			
93.7	47	6*d*				6*d*		
93.1	50				48			

continuum (20°K Single Crystal, 78°K Single Crystal)

continuum (20°K Conglomerate)

continuum (78°K Conglomerate)

TABLE I—(*Continued.*)

Angstroms	20°K Single Crystal Wave No.	Int.	20°K Conglomerate Wave No.	Int.	78°K Single Crystal Wave No.	Int.	78°K Conglomerate Wave No.	Int.
4492.1					55			
89.9	65.7	2*d*						
87.2	79.3	3*d*						
81.9	22305.5	3*d*						
4381.5	22817		22820		22820		22820	
79.7	26							
77.2	39	4*vd*			42.3	0*d*		
75.5	48							
75.3	49	*vd*						
70.7	73		22875					
69.8	78	5*s*	79	5*d*	22876	0*d*	77	2*d*
68.8	83		85					
63.9	22909	1*d*						
62.9	14	*vd*						
58.5	37	*vd*						
57.8	41	1*d*						
55.9	51	2*d*	53.5	3*d*				
54.2	60	*vd*						
51.0	77							
50.6	79	1*vd*						
48.5	90							
44.9	23009	0*d*						
43.2	18	*vd*	23015				23018	
			24					
			31	2*vd*				
40.8	31	2*vd*	44					
37.2	50	1*vd*						
33.4	70	0*vd*		1*vd*				1*vd*
33.0	72	*vd*						
30.4	86		91					
28.0	99	2*d*		2*vd*				
			23106					
25.0	23115	1*d*						
24.6	17		21				23120	
13.8			75	0*d*				
02.8			23234				35	
01.2			43					0*vd*
4298.8			56	1*vd*				
97.1			65				65	
73.6			93					
72.0			23401.5	0*d*				
70.1			12					
67.9			24	0*vd*				
59.4			71					
57.4			82	2*d*				
54.7			97					
49.4			23526					
48.3			32	1*d*				
44.2			55					
24.5			23665	0*vd*				
07.0	23763.0	1*s*	23763.4	6*vs*			23763.0	4*vs*
4189.8			23861	0*vd*				
83.7			95.5	0*d*				
75.1	23945		23946.5					
73.3	55	2*d*	52.5	3*d*			23953	2*d*
71.9	63		59					
64.3			24007					
62.2			19	1*vd*				

TABLE I—(*Continued.*)

Angstroms	20°K Single Crystal Wave No.	Int.	20°K Conglomerate Wave No.	Int.	78°K Single Crystal Wave No.	Int.	78°K Cnoglomerate Wave No.	Int.
4158.2			42	*vd*				
56.7	24051	0*d*	50	2*d*				
54.2			65	1*d*				
53.9			67	*vd*				
45.6			24115					
44.4			22	1*vd*				
42.5			33					
37.2			64	1*vd*				
34.7			79					
4096.2			24406	0*vd*				
86.2			66					
84.7			75	1*vd*				
83.5			82					
69.7			24565	0*d*				
58.0			24636	2*d*				
56.1			47					
50.6			80.5	1*d*				
48.3			95.0	0*d*				
20.0			24868.6	2*d*				

* Key to Tables I through IV. Boundaries of brackets indicate band edges. Edges of wide bands are very diffuse and their accuracy of measurement is correspondingly low. *s* indicates line with sharp edges, *d* =line with diffuse edges and *v* =very. Continuum is region of practically complete absorption and if band is included, band is very faintly discernible against continuous background. *h* indicates high temperature line. *x* indicates line originating from 110 cm^{-1} level, *y* =line from 235 cm^{-1} and *z* =line from 500 cm^{-1}.

TABLE I(*a*). *Frequencies of absorption lines of solid* $Pr_2(SO_4)_3 \cdot 8H_2O$.

Angstroms	105°K Wave No.	Int.	200°K Wave No.	Int.	300°K Wave No.	Int.	
6181			16173	0*vd*	16178	1*vd*	*hz*
73			94		96		
50			continuum ↓		16281	0*vd*	*hz*
36					93		
					continuum ↓		
4948			20206	0*vd*	20200	1*vd*	*hz*
42			30		30		
05	20382	0*vd*	20380		continuum ↓		*hz*
01	97			0*vd*			
00	20420	1*vd*					*hy*
4890	45		45				
83	20475	5*vd*	continuum ↓				*hy*
77	98						
71	20525	10*vd*					
61	65						
	continuum ↓						

thick. Both were photographed with the 3 meter concave grating spectograph of the California chemistry department which had a dispersion of about 5.4A per mm. All other plates reported were made on the grating of the Cornell physics department which had a dispersion of 4.63A per mm. The single crystals used here were about 1.6 mm thick and the conglomerate about 4 mm thick.

In both cases the salts were prepared by dissolving the oxides with dilute sulphuric acid and evaporating at room temperature until fairly large crystals formed. These were removed from the mother liquor, washed and dried between filter paper. In some cases the crystals were redissolved in distilled water and recrystallized but we were able to see no difference in the spectra when this was done. Experimentally we found it easier to obtain large crystals if a slight excess of acid was present. All plates were measured on the large comparator of the Cornell physics department. Photographs of the spectra were taken with the salt immersed in liquid hydrogen (20°K), liquid nitrogen (78°K), liquid methane (105°K), liquid ethylene (169°K), in CO_2 and acetone mixture (200°K)

and at room temperature (about 300°K). A description of the apparatus used in these investigations has been given elsewhere.[9] The frequencies of the lines are given in Table I. The accuracy of measurement of course varies with the region of the spectrum and the sharpness of the lines. For the very sharp lines at hydrogen temperatures the frequencies are probably good to 0.1 or 0.2 cm^{-1} while for the diffuse bands at room temperatures they may be in error as much as 15 cm^{-1}. In general the frequencies can be depended upon to about 2 cm^{-1}. A rough idea of the accuracy of measurement of the various lines can be obtained from Table I. The intensities given are only rough and

[9] Spedding and Bear, Phys. Rev. **42**, 58 (1932).

TABLE II.* *110 cm^{-1} levels.*

High temp. lines (78°K) Wave No.	Int.			Low temp. lines (20°K) Wave No.	Int.			$\Delta\nu$
16519, 43	1*vd*	(*r*)	(*c*)	16632	10*d*		(*c*)	110
16569, 87	4*vd*	(*r*)		16683, 86, 88	10*d*	(*r*)	(*c*)	115+
16632, 48	10*d*	(*r*)	(*s*)	16742, 45, 50	10*s*	(*r*)	(*s*)	110
16680, 16700	10*vd*	(*v*)	(*c*)	16790		(*r*)		
				16793	6*d*			
				16804	8*d*		(*s*)	110
				12.6, 13	10*d*			
20559	2*vd*		(*c*)	20667, 72	10*s*		(*c*)	110
20579, 83, 87	1*d*		(*c*)	20695.5	6*s*		(*c*)	110+
20604, 07, 13	8*vd*		(*c*)	20711, 16, 28, 32	6*d*, 8*d*		(*s*)	110, 115
20661, 66	8*d*		(*s*)					
76, 81	8*d*			20784	4*d*		(*c*)	110
21046, 59, 65	4*d*	(*r*)	(*c*)	21153, *57*, 62, 65	6*s*, 8*s*		(*s*)	110
21105, 10	8*vd*		(*c*)	21218, 21	5*d*, 5*d*		(*c*)	110+, 110
21176, 81	8*d*							
90, 21200	9*d*	(*v*)	(*s*)	21297	4*s*		(*s*)	110−
				21302	4*s*		(*s*)	110+
21227, 32	6*d*		(*s*)	21338	4*d*		(*s*)	110−
42, 46	5*d*			21349	2*d*		(*s*)	110−
				Average difference				110+

* Key to Tables II, III and IV. Where one side of a band increases markedly in intensity when the temperature of the absorber is raised, such an increase is shown by an "*r*" for the red side, or "*v*" for violet. Those lines which increase in intensity with increasing temperatures are called "high temperature" lines and the frequencies given are those at 78°K of the conglomerate unless marked (s) for single crystal. The low temperature lines are usually those given at 20°K, as they are much better resolved at this temperature and the shifts due to the contraction of the crystal are small between 20° and 78°K.

are to be depended on only for adjacent lines. No attempt has been made to compensate for different sensitivity of the plate to different frequencies, for different amounts of absorption in the glass apparatus or for the continuous absorption which sometimes overlies the discreet absorption. Thus, a line marked 1 or 2 in the center of an absorption band may be intensely absorbed, and nevertheless appear on the plate only faintly. Lines marked 0 appeared so faintly on the plate that they could not be seen under the comparator and had to be scratched before they could be measured. It should also be borne in mind that in the conglomerate the faintly absorbed lines are relatively much more enhanced that the strongly absorbed ones. As pointed out elsewhere,[10] the effect of photographing a conglomerate is to greatly increase the effective path length of absorption. With the strong lines the absorption is complete in a very thin layer of the solid. An increase in the

[10] Spedding and Bear, Phys. Rev. **39**, 15 (1932).

TABLE III. *235 cm⁻¹ levels.*

High Temperature (78°K) Wave Number		Int.		Low Temperature (20°K) Wave Number		Int.		$\Delta\nu$ cm^{-1}
16519 43	1*vd*	(*v*)	(*c*)	16769.4	6*vd*		(*c*)	230
16569 87	4*vd*	(*v*)	(*c*)	16790 *16813*	10*d*	(*v*)	(*s*)	235
20420 32 45	1*vd*	(105°K)	(*c*)	20667 72	10*d*		(*c*)	235+
				20710.6				
20475				16.3	6*s*			
87 98	5*vd*	(105°K)	(*c*)	*28.3* 32.4	8*s*		(*s*)	240
20528				20760.7	2*d*		(*s*)	235
37 45	10*d*			20773.5	3*d*		(*s*)	235
51	2*d*		(*c*)	20784.5	2*d*		(*s*)	235−
59	2*d*							
67	3*d*							
70								
20579								
83 87	1*d*		(*c*)	20816	5*s*		(*s*)	235−
				Average difference				235

TABLE IV. *500 cm⁻¹ levels.*

High Temperature (78°K) Wave Number	Int.			Low Temperature (20°K) Wave Number	Int.		$\Delta\nu$
16178 96	1*vd*	(300°K)	(*c*)	16684 85.5 88.4	8*s*	(*s*)	500
16281 93	0*vd*	(300°K)	(*c*)	16786	6*s*	(*s*)	500
20200 15 30	1*vd*	(300°K)	(*c*)	10 *20716* 28 32	6*s* 8*s*	(*s*)	500
20382 90 97	0*vd*	(105°K)	(*c*)	20878 82 86	3*vd*	(*c*)	490(?)
				Average difference			500

FIG. 1. 6000A band of $Pr_2(SO_4)_3 \cdot 8H_2O$ single crystal at 20°K.

thickness of the salt has no effect on the plate except to broaden the lines slightly. On the other hand with the weaker lines, increasing the thickness increases the absorption, and the intensity of the lines on the plate increases markedly. This relative enhancing of the weak absorption over the strong absorption in the conglomerates will frequently cause an apparent shift of the lines. If one is photographing an unresolved multiplet (brought about by oscillation frequencies, hyperfine structure[11] or Zeeman effect caused by paramagnetic atoms acting on each other) in which the outermost components are weak, the relative enhancing of these weak components will cause a shift in the center of density of the observed line. Thus, frequently a close doublet which is really the envelope of a more complicated structure will move closer together or farther apart when observed in a conglomerate.

A real shift also occurs with some of the lines when photographed at different temperatures. This is to be expected since the positions of the lines are dependent on the strength of fields present and these will change slightly as the crystal contracts with decrease in temperature.

The low lying excited levels were determined in two entirely independent ways. The first took advantage of the fact that the intensity of absorption is proportional to the number of atoms in the lowest state and that this in turn is proportional to the temperature according to the Boltzman relationship. As the temperature is lowered, at some critical point the lines originating from the lower state will suddenly fade out and from the temperature at which this fading occurs one can obtain a rough estimate of the separation of the levels from the basic state. Using this method we obtained positive evidence of excited states at about 100, 200 and 500 cm^{-1} above the basic one.

The second method depended on the fact that if absorption lines originating from the lower states terminate in common upper states, the interval of the lower states will be repeated throughout the spectra. Tables II, III and IV give evidence for these common intervals. The evidence here is not as conclusive as has been usual in the other rare earths. In the first place there are only two multiplets upon which it can be checked and in the second place the enormously enhanced intensity of the vibrational and oscillational frequencies which occur associated with the excited states in Pr caused hundreds of lines to lie close together. Thus one

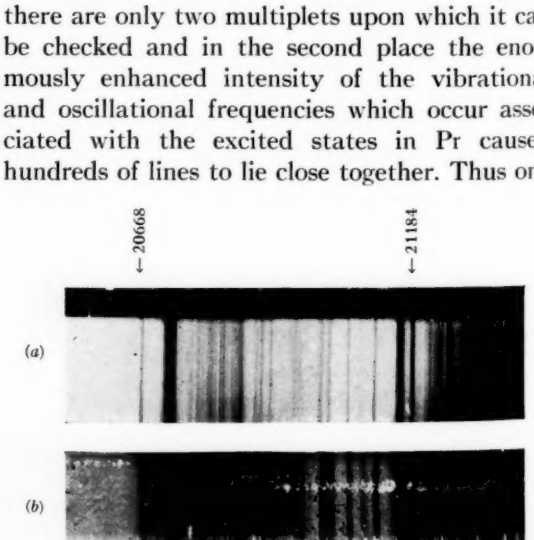

FIG. 2. 4800A band of $Pr_2(SO_4)_3 \cdot 8H_2O$; (*a*) single crystal at 20°K, (*b*) conglomerate at 20°K.

[11] If a $4f$ electron jumps outside the $5s\,5p$ shell the hyperfine structure will be quite large and may in a few cases be large enough to be resolved with the instrument used.

can take any frequency at random and find a number of such constant frequencies. However, in our opinion the frequencies we have reported are the correct ones. They account for *all* the high temperature lines and the agreement is by far the best we have been able to find. The low temperature lines associated with them are the more intense ones and are lines which can usually be traced from salt to salt. They therefore are probably due to crystal splitting rather than superimposed vibrational frequencies.

Figs. 1 and 2 show enlarged reproductions of the type of spectra observed.

Discussion of Results

It has been well established from magnetic and other considerations that the basic state of Pr ion in $Pr_2(SO_4)_3 \cdot 8H_2O$ is a $^3H_4$ arising from a $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^2 5s^2 5p^6$ electron configuration. Penney and Schlapp[3] making the assumptions that R. S. coupling is obeyed and that the crystalline fields of the surrounding atoms is predominantly cubic, have calculated that the basic state would be split into four levels situated at 0, 336*a*, 576*a* and 1296*a* where "*a*" is a constant dependent on the field strength. They evaluated "*a*" from the magnetic susceptibility measurements of Gorter and de Haas and found it to be equal to 0.293 cm^{-1}. Accordingly the levels would occur at 0, 98 cm^{-1}, 169 cm^{-1} and 379. One must be careful, however, in calculating the absolute values of the levels from the susceptibility measurements as the various investigators do not agree very well among themselves. If the field constant D is assumed to be the same for Pr as for Nd and the spectroscopic value is used for calculating "*a*" then the levels would occur as tabulated in Table V. There is a slight leeway in the calculations depending on the value of the screening constants used. In column 2 following Slater we have assumed that the 4*f* electrons have a screening constant value of 0.35. In column 3 we have arbitrarily reduced the field until the outside levels agree with the values found experimentally. The experimental values found here, column 3, are found to be in fair agreement with the calculated ones except for the contraction. One would expect, however, to find a slight distortion from the theoretical values because in the calculations all higher terms in the potential equation were neglected. These should be relatively more important for Pr than for Nd for the same reason that they were more important for $NdCl_3 \cdot 6H_2O$[12] than they were for $Nd_2(SO_4)_3 \cdot 8H_2O$,[5] for the homologous series of the rare earth sulphates breaks down between Pr and Ce. All the rare earths except La form hydrated sulphates containing 8 water molecules. La and Ce form hydrates containing nine. Thus as the rare earth ion gets larger due to lesser charge, the lattice slightly expands and with Ce and La the expansion has reached a point where an extra water molecule can enter the lattice. With Pr the expansion is not large enough to permit the extra water to enter but does give extra space into which the octahedron of oxygen atoms can expand. This will bring about a distortion of the field which in the case of $NdCl_3 \cdot 6H_2O$ made the higher terms in the potential equation more important and presumably would here also. In addition the weakening of the field would cause less over-all splitting of the levels as was found. We were able to find no evidence for splitting of the degenerate levels which would occur if rhombic terms were present. But we cannot be so positive of their nonexistence as we were in the case of Nd since the highly excited levels occur so close together that they might mask them.

The highly excited states may arise in either of two ways. The terms may arise from a $4fnx$ configuration when an electron is excited to a higher orbit, or they may arise from rearrangement of the $4f^2$ configuration. A number of authorities believe that all observed transitions are of this latter type and Van Vleck has summarized the arguments in favor of this

Table V.

1 From susceptibility measurements	2 From field constant D of Nd	3 Relative splitting	4 Found experimentally
cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
0	0	0	0
98	149	115	110
169	256	198	235
379	572	500	500

[12] Spedding and Hamlin, J. Chem. Phys. 5, 429 (1937).

TABLE VI.

Term	Crystalline		External
	Cubic Field	Rhombic Field	Magnetic Field
$^3H_4$	4	9	9
$^3H_5$	4	11	11
$^3H_6$	5	13	13
	13	33	33
$^3F_4$	4	9	9
$^3F_3$	3	7	7
$^3F_2$	2	5	5
$^3P_2$	1	5	5
$^3P_1$	1	3	3
$^3P_0$	1	1	1
$^1I_6$	6	13	13
$^1G_4$	4	9	9
$^1D_2$	2	5	5
$^1S_0$	1	1	1
	25	58	58

position.[8] If the transitions are of this "forbidden" type the number of excited states is extremely limited for a ^3H, ^3F, ^3P, ^1I, ^1G, ^1D and ^1S are the only terms permitted by the Pauli exclusion principle. The basic term is a $^3H_4$ so that transitions to the $^3H_5$ and the $^3H_6$ would certainly occur in the extreme infrared and would not be observed photographically. In Table VI the remaining terms are given with the number of components they would split into in a cubic field, in a field of very low symmetry and in a magnetic field. A number of these states would undoubtedly occur in the unphotographed regions of the spectra, particularly the infrared. Selection rules would also rule out transitions to some of them from the $^3H_4$. But even if all transitions were permitted and they all occurred in the observed bands, it is at once obvious that there are many more lines than can be explained on the basis of splitting alone. Ellis[13] takes the position that the violet bands are due to the transition $^3H_4$ to $^3P_0$, $^3P_1$ and $^3P_2$, respectively, and that the red band is a $^3H_4-{}^1I_6$. He bases his argument on a correlation with the La II spectra. This designation is attractive but immediately meets with serious difficulties. As can be seen from Table VII, P terms do not split in a cubic field and the I term gives rise to only six lines. All the remaining lines in these multiplets must therefore be due to vibrational or oscillational frequencies and many of these are of comparable intensity with the electronic levels so that there must be a strong coupling between the so-called crystal levels and the vibrational frequencies. It is then difficult in our present state of knowledge to understand why a strong coupling should take place with the ^1I and ^3P but not with the ^3H if all arose from the $4f^2$ configuration. Further, as one goes to rare earths with higher atomic number this coupling drops off very rapidly. It is definitely present in Nd for some multiplets, but the associated lines are much weaker. It can be observed for Sm only with very thick conglomerates and with Gd is not observed at all except for a very few lines which may or may not be of this type. If the electron jumps outside the completed $5s$ $5p$ shells, this behavior can be explained qualitatively because as one goes to rare earths of lighter atomic weight, a proportionally greater part of the electron cloud involved in the state is outside where strong coupling with the neighboring atoms can take place. We feel at present that the question regarding the nature of these states is still open and that very possible both types of transition occur.

A number of approximately constant frequency differences can be observed, particularly on the violet side of the bands, for example, Table VI. Also it should be pointed out that a number of more or less sharp lines on the violet side of the multiplets which are presumably

TABLE VII. *Typical example of type of frequency differences which occur in the bands.*

Single crystal at 20°K		
Wave Number	Int.	$\Delta\nu$(cm^{-1})
17105.0	$2vd$	
17161.3	$1d$	56
17211.4	$6s$	50
17264.5	$10s$	53
17325	(r)	60
32	$0vd$	
38		
17376.8	$0d$	52
17431	$0vd$	54
17486	$5d$	55
Average difference		54

[13] Ellis, paper in process of publication.

of vibrational origin are clearly present at 20° but rapidly vanish as the temperature is increased.

Not only do the lines vanish but the general absorption seems to vanish as well. This effect was present for Sm but is much more pronounced here. It would appear from this that as the crystal takes up vibratory motion a point is reached where sharp quantization of this vibratory motion suddenly disappears. For a proper study of this vibratory motion a number of plates should be taken at hydrogen temperatures using crystals and conglomerates of various thicknesses so that the spectra of each region could be studied under the most favorable conditions, but, unfortunately, liquid hydrogen is not at present available at Cornell.

We wish to express our thanks to Dr. Nutting, Dr. Meehan and Mr. Kraus of the University of California for their kindness in photographing the Pr at hydrogen temperatures. We also wish to thank Professor R. C. Gibbs for allowing us to use the facilities of the Cornell physics department.

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Energy States in Solids With Particular Reference to $NdCl_3 6H_2O$

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The absorption spectra of $NdCl_3 6H_2O$ has been photographed at 78°K, 169°K and 200°K. Two low lying excited states were found, located at 62 and 250 cm^{-1} above the basic state. These three levels presumably arise from a splitting of the basic state of $Nd^{+++}(^4J_{9/2})$ in a predominantly cubic field. The over-all splitting is slightly smaller than that which was found for the sulphate, and the relative splitting is slightly different. The differences reflect the change in crystal field which is brought about by the break in the homologous series of the hydrated chlorides of the rare earths between Nd and Pr.

THE atoms in a solid are so close together that they exert powerful electric fields on each other and thus cause the energy states of the atoms to split into a number of components. The nature of this splitting depends, of course, on the energy state involved and on the symmetry and position of the neighboring atoms in the solid. This problem has been treated theoretically by a number of investigators, notably Bethe[2] and Van Vleck.[3] Penney and Schlapp[4] have treated the specific case of $Nd_2(SO_4)_3 8H_2O$. They found that the variation of the experimental magnetic susceptibility with temperature could be accounted for very nicely if they assumed that the rare earth ions were surrounded by a cubic field, presumably brought about by the octahedron of oxygen atoms which surround the rare earth ion. They predicted that the basic state would split into three levels with a **relative** separation of 0, 243 and 834 cm^{-1}. Mr. Hamlin, Dr. Nutting and I investigated the salt spectroscopically and found three levels at 0, 77 and 260 which have the same relative separation as the levels predicted.[5] Further, using our values in Penney and Schlapp's equations, excellent agreement was obtained with the magnetic susceptibility measurements of a number of investigators.[5, 6]

In deriving their equations Penney and Schlapp used a potential energy function of the form $V=(x^4+y^4+z^4)$. They neglected all other terms, and the experimental results justified their being neglected. If any rhombic terms had

[1] Baker Research Fellow.
[2] Bethe, Ann. d. Physik **3**, 133 (1929).
[3] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932). Phys. Rev. **41**, 208 (1932), etc.
[4] Penney and Schlapp, Phys. Rev. **41**, 194 (1932).
[5] Spedding, Hamlin and Nutting, J. Chem. Phys. **5**, 191 (1937).
[6] Spedding, Phys. Rev. **50**, 574 (1936); Spedding, J. Chem. Phys. **5**, 160 (1937).

been present, one would have expected a further splitting of some of the levels and none was observed. The calculated splitting pattern of course depends directly on the nature of the potential equation used in the calculation. This equation itself is directly determined by the position and symmetry of the surrounding atoms. Thus, if one determines the splitting experimentally, then, theoretically, one should be able to determine the form of this equation and, therefore, the position and distance of the envelope of atoms surrounding the rare earth ion being studied. If this can be done, a powerful tool will be available to study short range order in a solid or solution, and it will be of assistance in x-ray studies in a region where such information can be obtained only with difficulty. The establishment of this tool, however, awaits the existence of more experimental data upon which it can be tested and we are making a systematic attempt to obtain such data. This paper is one of a series in which we are presenting the material obtained.

$NdCl_3 6H_2O$ crystallizes in the monoclinic system.[7] The six oxygens of the water molecules are almost certainly grouped about the Nd ion in the form of an octahedron so that the predominating field will be cubic and as a first approximation the splitting of the lowest state of the chloride should be the same as the sulphate. In the analogous case of the chloride and sulphate of Gd the fields are so similar that their spectra are almost identical.[8] In Nd, however, some differences would be expected, for if one examines the homologous series of the hydrated chlorides of the rare earths, one finds that they are all $6H_2O$ except Pr, Ce and La, which are $7H_2O$. This means that as the size of the rare earth ion increases due to a smaller total charge on the nucleus, the lattice slowly expands until with Pr it has become large enough to permit an extra water molecule to enter the lattice. In Nd, which is the next element to Pr in the series, the lattice evidently is not large enough to permit the extra water to be present, but there is extra space, which will permit the octahedron of water molecules to expand slightly into it. One would therefore predict that the over-all splitting of the lowest state of $NdCl_3 6H_2O$ would be somewhat smaller than the corresponding case of the $Nd_2(SO_4)_3 8H_2O$ (where the homologous series does not break down until La is reached). The distortion of the field which will take place when this occurs will, of course, have to be determined either from our experiments or from x-ray studies.

Experimental

The $NdCl_3 6H_2O$ was prepared from some fairly pure Nd supplied by Dr. H. N. McCoy. The chloride was prepared by dissolving the oxide in HCl and then slowly evaporating the solution at room temperatures until the salt crystallized out. This salt was recrystallized once from distilled water. Photographs were made of both a single crystal about $1\frac{1}{2}$ mm thick and of the conglomerate of small crystals 6 mm thick. The conglomerate has a tendency to bring out very faint lines, for, as has been pointed out elsewhere,[9] when light enters these small crystal fragments it is totally reflected a number of times before it emerges. As the refractive index of the salt increases very rapidly near an absorption band, the effective path length of light of that frequency would be very large. The strong absorption lines would appear about the same in both the single crystal and conglomerate, since the light in the center of the band would be completely absorbed in both cases. Increasing the path length of the light would therefore not have much effect on the plate except to broaden the line slightly. The very faint lines, however, would be much enhanced in the conglomerate over the single crystal, since the extra path length here would deepen the absorption as recorded by the plate.

All plates were photographed on a grating belonging to the physics department which had a dispersion of about 4.63A per mm. Plates were taken when the crystals were immersed directly in liquid nitrogen (78°K) and liquid ethylene

[7] Accurate crystallographic measurements have not been made for $NdCl_2 6H_2O$. However, they will not be very different from $SmCl_3 6H_2O$, which has axial ratios $a : b : c = 14713 : 1 : 12182$ and angle $= 86° 34'$. See "The Crystallography of Some Rare Earth Halides," Adolf Pabst, Am. J. Science, **22**, 426 (1931).

[8] Spedding and Nutting, J. Am. Chem. Soc. **55**, 496 (1933).

[9] Spedding and Bear, Phys. Rev. **39**, 948 (1932).

TABLE I.

	Nitrogen temperature 78°K				Ethylene 169°K		CO_2 acetone 200°K		
Single	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	Type
6838.1′ 6835.5 6838.1′	14,620.′ 14,625. 14,631.′	5*wd*			14,625.	2*d*			*h*
6814.2	14,671.	0*d*							*h*
6806.5	14,688.	3*s*			14,687.	3*d*			*l*
6797.4	14,707.	1*vd*							*h*
6786.9′ 6785.5 6784.1′	14,730.′ 14,733. 14,736.′	6*d*			14,731.	6*d*			*l*
6768.8	14,770.	5*d*			14,767.	5*d*			*l*
6755.8′ 6751.9 6748.1′	14,798.′ 14,807. 14,815.′	7*wvd*			14,793.′ 14,808. 14,822.′	6*d*			
6728.3′ 6726.1 6723.7′	14,859.′ 14,863. 14,869.′	6*vd*			14,850.′ 14,866. 14,886.′	6*d*			
							15,663.′ 15,678. 15,716.′	0*vwd*	*h*
			15,746.	0*vd*	15,737.′ 15,746. 15,758.′	1*d*	15,735.′ 15,747. 15,760.′	1*wd*	*h*
					15,766.′ 15,773. 15,781.′	0*d*	15,768.′		*h*
			15,800.	1*d*	15,789.′ 15,802. 15,816.′	1*d*		*vwd*	*h*
			15,813.	0*d*					*h*
			15,825.	2*d*	15,825.	0*d*	15,824.′		*h*
			15,842.	1*d*					
6303.6	15,860.	2*d*	15,858.′ 15,861. 15,864.′	5*d*	15,863.	2*d*	15,853.′ 15,860. 15,870.′	2*wd*	*l*, *h*
			15,875.	3*d*	15,877.	1*s*			*l*, *h*
6293.1	15,886.	4*s*	15,887.	10*s*	15,888.	3*s*	15,883.′ 15,887. 15,892.′	2*d*	*l*
6279.7′ 6278.9 6278.1′	15,920.′ 15,922. 15,924.′	8*s*	15,916.′ 15,922. 15,927.′	10*d*	15,918.′ 15,923. 15,928.′	8*d*	15,916.′ 15,924. 15,930.′	9*d*	*l*
6273.1	15,937.	5*s*	15,934.′ 15,938. 15,941.′	10*d*	15,934.′ 15,938. 15,941.′	7*d*	15,931.′ 15,937. 15,942.′	7*d*	*l*
6264.3	15,959.	2*d*	15,956.′ 15,959. 15,962.′	6*d*	15,961.	3*d*	15,954.′ 15,960. 15,966.′	4*d*	*h*

TABLE I.—*Continued.*

	Nitrogen temperature 78°K				Ethylene 169°K		CO_2 acetone 200°K		
Single	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	Type
6254.5′ 6252.8 6251.0′	15,984.′ 15,989. 15,993.′	3*d*	15,984.′ 15,991. 15,998.′	7*d*	15,984.′ 15,991. 15,998.′	4*d*	15,980.′ 15,991. 16,000.′	5*wd*	*l*
6241.7′ 6240.3 6238.9′	16,017.′ 16,021. 16,024.′	6*d*	16,013.′ 16,021. 16,028.′	9*wd*	16,016.′ 16,021. 16,025.′	8*d*	16,014.′ 16,022. 16,028.′	8*d*	*l*
6229.7′ 6228.6 6227.6′	16,048.′ 16,051. 16,053.′	4*d*	16,046.′ 16,051. 16,056.′	8*d*	16,050.	5*d*	16,042.′ 16,050. 16,055.′	5*d*	*l*
							16,071.′ 16,076. 16,082.′	2*d*	
			16,692.	0*d*					*h*
			16,705.	0*d*					*h*
5968.0	16,752.	2*d*	16,755.	4*d*					*l*
5962.3	16,768.	1*vd*	16,767.	3*d*					*l*
5822.9	16,879.	3*vd*	16,877.′ 16,885. 16,891.′	4*d*					*h*
5912.3	16,909.	3*vd*	16,906.′ 16,911. 16,918.′	5*d*					*h*
			16,918.′ 16,926. 16,936.′	3*dw*					
			16,944.′ 16,955. 16,969.′	1*ws*					
			16,979.	2*d*					
			17,021.	2*d*					
			17,047.′ 17,056. 17,064.′	3*wd*					
5856.7	17,070.	8*s*	17,064.′ 17,070. 17,076.′	8*s*					*h*
5850.1 5846.6 5843.3	17,089.′ 17,099. 17,109.′	7*wd*	17,080.′ 17,099. 17,117.′	6*vwd*					*h*
5835.9	17,131.	9*s*	17,127.′ 17,131. 17,136.′	9*d*					*l*
5830.7′ 5817.6′	17,146.′ 17,185.′	8*vws*	17,144.′						*l*
5813.8	17,196.	5*s*							

TABLE I.—*Continued.*

	Nitrogen temperature 78°K				Ethylene 169°K		CO_2 acetone 200°K		
Single	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	Type
5812.0′ 5786.6′	17,201.′ 17,276.′	7*vwd*							
5781.9′ 5775.9′	17,291.′ 17,309.′	8*ws*							
5771.6′ 5765.1′	17,321.′ 17,341.′	8*wd*		6*vwd*					
5758.7	17,360.	8*d*							
5747.8′ 5737.9′	17,393.′ 17,423.′	7*vwd*							
5734.1′ 5708.2′	17,435.′ 17,514.′	7*vwd*	17,526.′						
			17,539.′ 17,548. 17,555.′	5*wd*					
			17,567.′ 17,573. 17,580.′	5*wd*					
			17,615.′ 17,678.′	4*vwd*					
			17,694.′ 17,703. 17,712.′	2*wd*					
			18,652.	0*d*	18,640.′ 18,655. 18,666.′	3*vd*			
			18,686.	0*d*	18,680.′ 18,693. 18,707.′	2*vd*			
			18,752.	2*d*	18,745.′ 18,753. 18,763.′	3*vd*			*h*
			18,786.	3*d*	18,778.′ 18,789. 18,804.′	3*vd*			
			18,818.	1*d*					
			18,847.	2*d*	18,842.′ 18,850. 18,860.′	2*vd*			
			18,865.	0*d*					
			18,898.	0*wd*	18,882.′ 18,893.′ 18,903.′	2*vd*			
			18,920.′ 18,925.	3*d*					
5279.8′ 5278.1 5376.8′	18,935.′ 18,941. 18,946.′	8*d*	18,933.′ 18,940. 18,945.′	8*d*	18,920.′ 18,934. 18,953.′	3*vd*			*h*

TABLE I.—*Continued.*

	Nitrogen temperature 78°K				Ethylene 169°K		CO_2 acetone 200°K		
Single	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	Type
5271.0′	18,966.′								
5270.3	18,969.	10*s*	18,967.	8*s*	18,965.′				
5269.2′	18,973.′				18,976.	3*vd*			
5268.3	18,976.	10*s*	18,976.	8*s*	18,985.′				
5267.6′	18,979.′								
5261.2	19,002.	10*vs*	19,001.	10*s*	18,999.	3*d*			*l*
5254.6′	19,026.′		19,014.′		19,015.′				
5253.1	19,031.	9*d*							
5251.7′	19,037.′			8*vwd*		3*vd*			
5250.3	19,041.	9*d*							
5248.9′	19,046.′		19,056.′		19,056.′				
5240.0′	19,079.′		19,071.′						
5238.6	19,084.	7*d*	19,078.	7*d*					
5237.4′	19,088.′		19,085.′						
					19,072.′				
					19,088.	3*vd*			
					19,109.′				
5236.3′	19,092.′		19,087.′						
5234.9	19,097.	9*d*	19,096.	8*wd*					
5233.3′	19,103.′		19,105.′						
			19,115.	5*d*					
5227.3′	19,125.′		19,121.′		19,123.′				
5225.9	19,130.	4*vd*							
5224.6′	19,135.′								
5223.7	19,138.	10*vd*							
5222.3′	19,142.′			8*vwd*		3*vd*			
5221.2′	19,147.′								
5219.9	19,152.	10*vd*							
5218.8′	19,156.′								
5216.3	19,165.	4*vd*							
5213.7′	19,175.′		19,177.′		19,183.′				
5207.3′	19,198.′		19,194.′		19,193.′				
5204.5	19,209.	3*wd*	19,209.	6*wd*	19,210.	2*vd*			
5201.4′	19,220.′		19,221.′		19,226.′				
			19,311.	2*d*	19,266.′				
5164.5	19,357.	3*d*	19,358.	6*d*		3*vd*			
					19,375.′				
			19,400.	1*d*					*h*
			19,417.	3*d*					*h*
5139.3	19,452.	3*d*	19,451.	6*d*	19,441.′				
5136.0	19,465.	4*d*	19,463.	7*d*					*l*
5132.1	19,479.	4*d*	19,479.	6*d*					*l*
5126.0′	19,503.′		19,495.′						
5122.0	19,518.	10*wd*							
5118.6′	19,531.′			6*vwd*		3*vd*			
5117.1′	19,537.′								
5115.8	19,542.	10*s*							
5114.3′	19,548.′		19,550.′						
5106.7′	19,576.′		19,572.′						
5104.5	19,585.	9*wd*	19,586.	5*vwd*					
5102.0′	19,594.′		19,601.′						

TABLE I.—*Continued.*

	NITROGEN TEMPERATURE 78°K				ETHYLENE 169°K		CO_2 ACETONE 200°K		
SINGLE	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	TYPE
					19,613.′				
5094.9′	19,622.′		19,625.′		19,623.′				
5092.3	19,632.	7*wvd*							
5089.6′	19,642.′			5*vwd*					
5087.3	19,651.	2*wvd*				3*vd*			
5084.9′	19,660.′		19,659.′						
5082.1	19,671.	1*vd*	19,671.	4*d*					
					19,696.′				
			19,733.	2*d*					
					19,793.′				
5039.2′	19,839.′		19,835.′						
5036.5	19,849.	6*wd*	19,846.	5*wd*					
5034.0′	19,860.′		19,857.′						
5023.5′	19,900.′		19,886.′						
5021.0	19,911.	8*wd*	19,908.	6*vwd*		3*vd*			
5018.6′	19,920.′		19,927.′						
			19,949.′						
5007.8	19,963.	2*vd*	19,969.	4*vwd*					
			19,990.′						
					20,001.′				
			20,053.	2*vd*					
			20,199.	1*vd*					
			20,211.	0*vd*					
			20,324.	2*vd*					
			20,390.	3*d*					
			20,414.′		20,414.′				
			20,427.	4*wd*	20,427.	2*vd*			
			20,437.′		20,441.′				
			20,451.′		20,453.′				
			20,457.	4*d*					
			20,466.′						
			20,473.′						
			20,480.	5*d*		3*vd*			
			20,484.′						
			20,491.′						
			20,498.	5*wd*					
			20,505.′		20,506.′				
			20,516.′						
			20,523.	5*wd*					
			20,531.′						
			20,543.′		20,545.′				
			20,558.	5*vwd*	20,558.	3*vd*			
			20,573.′		20,571.′				
			20,588.′		20,583.′				
			20,597.	5*wd*					
			20,606.′						
					20,611.	1*vd*			
			20,616.′						
			20,625.	5*wd*					*h*
			20,635.′		20,634.′				

TABLE I.—*Continued.*

	NITROGEN TEMPERATURE 78°K				ETHYLENE 169°K		CO_2 ACETONE 200°K		
SINGLE	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	TYPE
4838.8	20,661.	9*vs*	20,660.	8*s*	20,664.	7*d*			
			20,672.	8*s*	20,677.	7*d*			
			20,684.′ 20,695. 20,705.′	3*wd*					
			20,721.′ 20,727. 20,734.′	3*d*					
					20,755.′ 20,764. 20,771.′	4*vd*			*h*
4808.5′ 4805.9 4802.5′	20,791.′ 20,802. 20,817.′	1*wd*	20,781.′ 20,802. 20,820.′	5*vwd*	20,782.′ 20,799. 20,813.′	6*vd*	20,780.′		*h*
4799.6′ 4797.4 4795.3′	20,830.′ 20,839. 20,848.′	1*wd*	20,827.′ 20,837. 20,848.′	5*wd*	20,833.′ 20,856.	9*vd*			*h*
4792.2′ 4791.1 4789.5′	20,862.′ 20,866. 20,874.′	1*d*	20,856.′ 20,870. 20,887.′	5*wd*	20,883.′				*l*
			20,908.	1*vd*					
4773.0′ 4772.2 4771.4′	20,945.′ 20,949. 20,953.′	9*d*	20,928.′ 20,949. 20,963.′	7*vwd*	20,930.′	8*vd*		2*vwd*	*h*
4766.9′ 4766.0 4765.1′	20,972.′ 20,976. 20,981.′	8*s*	20,969.′ 20,976. 20,984.′	7*wd*	20,991.′				*h*
4758.3	21,010.	8*vs*	21,009.	8*s*	21,014.	8*s*			*l*
4757.0	21,016.	9*vs*	21,017.	8*s*			21,033.′		*h*
4752.0	21,038.	5*s*	21,032.′ 21,038. 21,043.′	8*s*	21,040.	8*s*	21,034.	4*d*	*l*
4743.0	21,078.	9*s*	21,070.′ 21,080. 21,096.′	7*wd*	21,070.′ 21,079. 21,090.′	7*vd*	21,064.′ 21,080. 21,094.′	4*vwd*	*l*
4732.8′ 4731.3 4730.0′	21,124.′ 21,130. 21,136.′	7*d*	21,109.′ 21,128. 21,143.′	7*vwd*	21,115.′ 21,132. 21,151.′	7*vd*	21,112.′ 21,129. 21,153.′	4*vwd*	
4717.3 4715.7	21,193. 21,200.	5*d* 9*s*	21,183.′ 21,189. 21,204. 21,210.′	7*vwd* 7*vwd*	21,189.′ 21,201. 21,211.′	6*vd*	21,178.′ 21,194. 21,208.′	4*vwd*	
4708.9	21,231.	2*d*							
4698.9′ 4697.3 4695.6′	21,276.′ 21,283. 21,291.′	9*wd*	21,232.′ 21,284.′	7*vwd*	21,238.′ 21,264. 21,290.′	8*vd*	21,235.′ 21,255. 21,278.′	4*vwd*	
			21,299.	2*d*					

TABLE I.—*Continued.*

	Nitrogen temperature 78°K				Ethylene 169°K		CO_2 acetone 200°K		
Single	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	Type
4689.3	21,319.	2*d*	21,322.	3*d*	21,322.	1*d*	21,315.	4*d*	
4682.1′ 4681.2 4680.2′	21,352.′ 21,357. 21,361.′	7*d*	21,346.′ 21,356. 21,368.′	7*wd*	21,349.′ 21,358. 21,367.′	8*d*	21,358.	4*d*	
4674.3	21,388.	3*d*	21,392.	5*d*	21,392.	4*d*			
4666.7	21,423.	2*d*	21,425.	4*d*	21,425.	3*d*			
4660.2	21,453.	6*s*	21,445.′ 21,453. 21,462.′	6*wd*	21,453.	6*d*			
4653.1	21,485.	2*d*	21,477.′		21,481.′		21,456.′		
4647.4	21,512.	2*d*							
4641.1′ 4638.4 4636.1′	21.541.′ 21,553. 21,564.′	7*wd*			21,555.	9*d*			
4632.5	21,581.	1*d*		*vwd*				8*vwd*	
4629.0	21,597.	1*d*							
4617.3	21,652.	2*wd*			21,674.	9*vd*			
4608.5	21,693.	2*d*							
			21,733.′		21,733.′		21,717.′		
			21,773.	4*d*	21,779.	1*d*			
4569.8′ 4567.8 4565.8′	21,877.′ 21,886. 21,896.′	8*wd*	21,821.′ 22,000.′	7*vwd*	21,850.′ 21,900. 21,952.′	8*vd*	21,830.′ 22,003.′	8*vwd*	
			22,092.′	3*vwd*	22,035.′ 22,066. 22,102.′	1*vd*			
			22,153.	1*vd*					
			22,258.	1*vd*					
			22,290.′ 22,301. 22,310.′	3*wvd*					*h*
4474.3′ 4473.4 4472.4′	22,343.′ 22,348. 22,353.′	6*d*	22,335.′ 22,358. 22,381.′	8*vwd*	22,338.′ 22,366. 22,391.′	8*vd*	22,335.′ 22,364. 22,388.′	7*vwd*	*l*
4470.2′ 4469.1 4468.0′	22,364.′ 22,369. 22,375.′	6*d*	22,408. 22,418.	2*vd* 2*vd*					
4448.5	22,473.	4*d*	22,429.′ 22,475. 22,487.′	6*vwd*	22,462.′ 22,478. 22,491.′	4*vd*	22,455.′ 22,479. 22,494.′	3*vwd*	
4439.8	22,517.	2*d*	22,503.′ 22,517. 22,528.′	4*wd*	22,509.′ 22,528. 22,546.′	2*vd*	22,511.′ 22,532. 22,557.′	3*vwd*	
					22,975.	1*d*	22,976.	1*d*	*h*

TABLE I.—*Continued.*

	Nitrogen temperature 78°K				Ethylene 169°K		CO_2 acetone 200K°		
Single	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	Type
4339.8	23,036.	2*d*	23,032.′ 23,039. 23,045.′	4*d*	23,027.′ 23,040. 23,053.′	8*d*	23,015.′ 23,052.′	9*vwd*	*l*, *h*
4332.4	23,075.	2*d*	23,067.′ 23,081. 23,092.′	4*wd*	23,064.′ 23,079. 23,092.′	8*d*	23,063.′		*h*
			23,099.	3*s*	23,100.	6*d*		8*vwd*	*h*
					23,112.′ 23,124. 23,137.′	2*d*	23,111.′		
			23,159.	2*d*	23,143.′ 23,154. 23,164.′	3*d*	23,154.	0*vd*	
			23,185.	1*d*	23,170.′ 23,184. 23,193.′	2*d*			
4304.8	23,223.	7*s*	23,216.′ 23,224. 23,231.′	9*ws*	23,214.′ 23,226. 23,237.′	10*d*	23,205.′ 23,224. 23,243.′	9*vwd*	*h*, *l*
					23,214.′ 23,226: 23,237.′	10*d*			
4293.5	23,285.	10*s*	23,269.′ 23,286. 23,307.′	8*wvs*	23,266.′ 23,287. 23,307.′	10*d*	23,260.′ 23,287. 23,313.′	10*vwd*	*l* *l*
			23,324. 23,339.′	2*wd*	23,323. 23,339.′	2*d*			
			23,351.	2*s*	23,347.	2*d*			*l*
			23,363.	3*s*	23,359.	2*d*			
4274.3	23,389.	3*vd*	23,373.′ 23,389. 23,402.′	7*vwd*	23,380.′ 23,390. 23,402.′	6*d*	23,397.	10*d*	
			23,410.′ 23,412. 23,415.′	2*d*					
			23,435.	3*d*	23,422.′ 23,430. 23,438.′	1*s*			
			23,452.	2*d*	23,452.	0*d*			
			23,471.	3*s*					
			23,482.	3*d*	23,462.′ 23,481. 23,494.′	1*s*			
			23,497.	3*d*					
			23,505.′ 23,522. 23,543.′	2*vwd*	23,505.′ 23,523. 23,538.′	0*s*			
			23,550.′ 23,559. 23,573.′	2*wd*					

TABLE I.—*Continued.*

	Nitrogen temperature 78°K				Ethylene 169°K		CO_2 acetone 200°K		
Single	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	Type
4238.8	23,585.	1*vd*	23,584.′ 23,597. 23,607.′	4*wd*	23,591.	2*vd*	23,586.	1*d*	
			23,612.′ 23,622. 23,630.′	2*wd*					
			23,639.′ 23,658. 23,675.′	2*vwd*					
4218.6	23,698.	4*s*	23,694.′ 23,699. 23,703.′	5*s*	23,697.	4*d*	23,697.	1*d*	*h*
4207.8	23,759.	9*vs*	23,747.′ 23,759. 23,770.′	8*wd*	23,747.′ 23,759. 23,771.′	10*vd*	23,750.′ 23,759. 23,770.′	4*wd*	*l*
4201.8	23,792.	3*vd*	23,787.′ 23,801. 23,814.′	4*dw*	23,786.′ 23,801. 23,816.′	4*vd*	23,789.′ 23,800. 23,812.′	2*wd*	*h*
4190.5	23,857.	3*vd*	23,848.′ 23,862. 23,875.′	4*dw*	23,859.	3*vd*	23,838.′ 23,857. 23,862.′	1*wd*	*l*
4180.3	23,915.	5*d*	23,902.′ 23,912. 23,922.′	6*dw*	23,902.′ 23,913. 23,922.′	8*d*	23,902.′ 23,914. 23,922.′	5*wd*	
			23,930.	3*d*		2*d*			
			23,950.	3*d*	23,953.′		23,949.	0*d*	
4159.1	24,037.	1*d*	24,042.	4*s*	24,039.	1*d*			
4153.2	24,071.	3*s*	24,074.	6*s*	24,072.	7*d*	24,069.	3*d*	
			24,378.	0*d*					
			24,408.	0*d*					
4073.5	24,542.	3*s*	24,543.	6*s*	24,544.	7*s*	24,544.	3*d*	
			24,617.	2*s*					
			24,635.	1*d*					
			24,651.	1*d*					
			24,698.	0*d*	24,699.	1*vd*	24,698.	1*d*	
			24,757.	0*d*	24,756.	1*vd*	24,750.	1*d*	
4025.4	24,835.	8*s*	24,837.	8*s*	24,831.′ 24,838. 24,844.′	10*s*	24,830.′ 24,837. 24,844.′	7*d*	
4013.7	24,908.	7*s*	24,908.	8*s*	24,907.	10*d*	24,900.′ 24,913.	6*wd*	
4012.1	24,917.	7*s*	24,918.	8*s*	24,916.	10*d*	24,924.′		
			24,927.	3*s*					

TABLE I.—*Continued.*

	NITROGEN TEMPERATURE 78°K				ETHYLENE 169°K		CO_2 ACETONE 200°K		
SINGLE	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	TYPE
			24,947.	4*s*	24,945.	0*d*			
3830.3	26,100.	3*s*	26,105.	5*s*			26,099.	3*d*	
3821.4	26,162.	10*s*	26,163.	5*s*			26,159.	3*d*	
			26,250.	5*s*					

′ =band edge, *d* =diffuse, *vd* =very diffuse, *w* =wide about 15 cm^{-1}, *s* =sharp edges, *h* =line originating from low excited level, *l* =line originating from basic state.

(169°K) also at 200°K. A detailed description of the apparatus used in the photographing has been given elsewhere.[10]

The wave-lengths of the lines observed with their corresponding intensities are given in Table I. The intensities are based on an arbitrary scale of 0–10 and are of value only with regard to relative intensities of adjacent lines. Those marked 0 were so faint that they could not be seen under the comparator and had to be scratched with a needle under an eyeglass. Those marked with intensity 1 could be faintly seen under the comparator but were also scratched in order to locate them. All lines with intensity greater than 5 probably show complete absorption in the centers. Numbers above 5 merely indicate that the absorption is probably greater for the higher numbers, as the wings of the lines are better developed. It cannot be emphasized too strongly that the intensities given are only good for relative intensities of lines in the same region of the plate. Thus, in the regions of the plate where the background is weak due to lack of sensitivity of the plate, general absorption of the glass apparatus or to other causes, a line in which complete absorption takes place may be barely visible and therefore marked 2 or 3. The accuracy of measurement of the lines varies a great deal with the sharpness of the line, the region of the plate, etc. A general idea of the accuracy of measurement of each line can be obtained from Table I. In general, however, the frequencies can be depended upon to about 2 cm^{-1}. The absorption lines seem to originate from at least three lower states located at 0, 62 and 250 cm^{-1}. These lower levels were located by two entirely independent methods. The first took advantage of the fact that the intensity of absorption line is proportional to the number of atoms in the lower state. These in turn are proportional to the temperature according to the Boltzman relationship. Therefore, the lines originating from a low lying excited state will suddenly fade out at some critical point as the temperature is lowered. From the temperature at which the lines fade out one can calculate roughly the separation of the levels. The second method takes advantage of the fact that if lines originating from the lower levels terminate in common upper levels the interval separations of the lower states will be repeated throughout the spectra. Tables II and III present some of the most striking cases of this constant interval repetition. The existence of the upper level was

[10] Spedding and Bear, Phys. Rev. **42**, 58 (1932).

TABLE II. *Neodymium chloride −62 cm^{-1} levels.* (*Nitrogen conglomerate unless otherwise noted.*)

14,625 (*xl*)	−14,688 (*xl*)	63	
14,671 (*xl*)	−14,733 (*xl*)	61	
14,707 (*xl*)	−14,770 (*xl*)	63	
15,800	−15,861	61	?
15,813	−15,875	62	?
15,825	−15,887	62	
15,861	−15,922	61	
15,875	−15,937	62	
15.959	−16.021	62	
16,692	−16,755	63	
16,705	−16,767	62	
17,070	−17,131	61	
17,099	−17,161	62	
18,940	−19.001	61	
19,400	−19,463	63	
19,417	−19,479	62	
20,949	−21,009	60	
20,976	−21,038	62	
21,017	−21,080	63	
23,224	−23,286	62	
23,699	−23,759	60	
23,801	−23,862	61	

xl =single crystal.

absolutely certain as it is plainly evident by method 1. But it should be pointed out that the constant interval separation for these high levels is very difficult to locate, for as a rule at the temperature at which the lines from the excited state become intense all of the lines have become diffuse due to temperature broadening. The constant interval separation is made even more difficult to determine by the fact that the excited states in the multiplet occur close together and when the lines are broad the lines in the multiplets tend to fuse together. Nevertheless, we feel fairly confident that the upper state is located at 250 cm^{-1}.

Discussion of Results

Second-order terms in the potential equation would be manifested by a further splitting of the 62 cm^{-1} and the 250 cm^{-1} levels. We were unable to detect any such splitting and unless unusual selection rules which would forbid all transitions to any upper state were operative, no splitting greater than 2 or 3 cm^{-1} occurred. Such selection rules seem unlikely and we concluded, therefore, that any second-order terms which might exist in the potential equation must be small. The rhombic splitting could not be greater than 1 or 2 percent of the cubic splitting. The over-all splitting of the basic state as might be expected was less than that for the sulphate. The octahedron of oxygens presumably had expanded into the hole in the lattice and the fields about the Nd were thereby weaker. The relative separation of the lower levels was slightly different from that calculated by theory and found for the sulphate. The higher order terms in the potential equation, which it was found possible to neglect in the sulphate, were evidently more important here due to the distortion.

Table III. *Neodymium chloride −250 cm^{-1} levels. (169 degrees unless otherwise noted.)*

15,663′ (200 degrees)		
15,678	−15,924	
15,716′	−15,937	
15,746	−15,991	245
15,773	−16,021	248
15,802	−16,050	248
16,885 (nit)	−17,131 (nit)	246
16,911 (nit)	−17,161 (nit)	250
18,753	−18,999	246
20,625 (nit)	−20,870 (nit)	245
20,764	−21,009 (nit)	245
20,782′		
20,799	−21,040	
20,813′		
20,833′		
20,856	−21,079	
20,883′		
22,975	−23,226	251
23,040	−23,287	247
23,079	−23,323	244
23,100	−23,347	247

nit = 78°K.

The excited multiplets experimentally can be divided into two groups. The first, as exemplified by the 14,700 and 15,800 cm^{-1} multiplets, consists of a few intense lines by themselves. The second group exemplified by the 17,000, 18,000 and 19,000 cm^{-1} multiplets consists of a number of intense lines associated with a large number of fainter ones. These fainter lines are so close together that with thick conglomerates they tend to fuse together to give a continuum. They resemble the band lines which one observes in polyatomic molecules and presumably are due to superimposed vibrational frequencies. Even with thick conglomerates no evidence of these associated lines has been found for the red multiplets. On the other hand, in the violet, certain multiplets which resemble the first type do show faintly some associated lines when very thick conglomerates are used. Whether or not these associated lines appear is not a matter of relative intensities, for the 14,600 multiplet is one of the most intense in the spectra, since it can be detected when only minute quantities of Nd salt are present and when most of the other multiplets are completely invisible.

An excited state can arise in either of two ways. First it can be a "forbidden" transition of the type $4f^3-4f^3$. Van Vleck[11] has discussed this type of transition in detail and believes that the observed transitions are all of this type. With the present state of theory a number of difficulties arise if one takes this position. For example, the number and position of the excited states are not in good agreement with it. Since the basic and excited states both arise from the same electronic configuration, the potential field equation for both states should be the same and as the number of excited states is limited by

[11] J. H. Van Vleck, J. Phys. Chem., Jan. (1937).

Pauli's principle one can calculate the splitting patterns for these various states. In the sulphate the agreement with excited states was not good even though it was excellent for the lowest state. There were always too many lines in the multiplet, and usually the intervals and over-all separations were wrong. In a few cases, e.g., in the 14,600 multiplet the splitting pattern of five of the six lines could be considered in very fair agreement with some of the possible states ($^2K_{15/2}$ or $^2L_{15/2 \text{ or } 17/2}$) but the sixth line which had to be neglected was one of the most intense in the group and differed in no way from the others. Also, the matrix coefficients q were very different from that required.

The second possibility is that the transition would be of the type $4f^3-4f^25x$. This supposition is attractive for the second type of multiplet as one would expect the vibrational frequencies to couple with the electron frequency more readily if one of the electrons were outside the completed $5s$ $5p$ shells. This idea is further borne out by the fact that so far we have not found any vibrational states associated with the lower states and that these associated lines are most pronounced in Pr where only two electrons give rise to the multiplets. On the other hand this supposition as pointed out by Van Vleck[11] is open to serious objections such as wrong order of intensity of lines, etc.

We shall discuss the problem of the excited states in much more detail in a later paper as we feel that the problem requires more experimental data before it can be discussed profitably. We have photographed a number of salts in which the potential fields are slightly different and by studying how the excited levels vary from salt to salt we hope to be able to learn a good deal more about the nature of these states.

We wish to thank Dr. H. N. McCoy for his generous gift of the Nd salt used in these investigations and Professor Gibbs of the physics department for extending to us the facilities of his department.

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The Normal Vibrations and the Vibrational Spectrum of C_2H_6*

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An investigation is made of the vibrations, frequencies and selection rules of C_2H_6, which is assumed to have an internal rotational degree of freedom subject to a restricting potential of an arbitrary magnitude. Making use of the fact that the total potential energy of such a molecule is invariant under a reflection in a plane perpendicular to the threefold symmetry axis, a set of vibrational selection rules is obtained which is more complete than that of Teller and Topley who made use only of the invariance of the potential energy under operations of the point group D_3. The vibrational selection rules are found to be essentially the same for all degrees of restriction of the internal rotation except for the rules governing the appearance of the degenerate frequencies in the Raman spectrum, so that even in the limit of free rotation only one type of degenerate vibrational frequency is active in the infrared spectrum. A normal coordinate treatment based on a three-constant potential function of the valence force type is found to give a set of frequencies in good agreement on the whole with the observed frequencies. The fundamental region of the vibrational spectrum seems to afford no conclusive evidence for or against free internal rotation.

IN the present paper a theoretical study is made of the vibration spectrum of C_2H_6 in which there is assumed to be a potential of an arbitrary magnitude restricting the internal rotation. Previous to this, Sutherland and Dennison[1] have calculated the frequencies of the nondegenerate vibrations upon the assumption that forces between distant H atoms can be neglected, and

* A preliminary report of this study was given at the Washington meeting of the American Physical Society, April, 1936 (see Phys. Rev. **49**, 881 (1936)) and in a Letter to the Editor, Phys. Rev. **51**, 53 (1937).

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[1] Sutherland and Dennison, Proc. Roy. Soc. **A148**, 250 (1935).

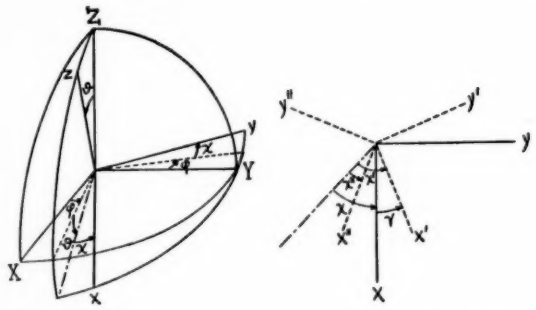

FIG. 1. (a) Diagram of x, y, z axes showing Eulerian angles. (b) Diagram of x, y plane showing relations of x', y' and x'', y'' axes. $\chi=(\chi'+\chi'')/2$ and $\gamma=(\chi'-\chi'')/2$.

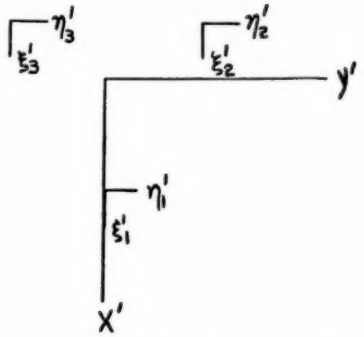

FIG. 2. Projection of H' (H'') plane onto x', y' (x'', y'') plane showing vibrational coordinates.

Teller and Topley[2] have assigned frequencies to the normal vibrations in the light of interpretations of the spectra of related molecules and the specific heat of C_2H_6. In the paper following, which we shall refer to henceforth as II, the rotational structure of the vibration bands is examined and an estimate is made of a lower limit to the potential restricting internal rotation.

Coordinate System

It will first be necessary to specify the rotational and vibrational coordinate systems to be used in the present and the following paper. Figs. 1a and 1b illustrate the rotational coordinates. Single and double primes are used throughout to distinguish coordinates referring to the two CH_3 groups. Two rotating systems of axes x', y', z' and x'', y'', z'' are chosen with a common origin at the center of gravity of the whole molecule, each system defining the equilibrium position of a CH_3 group. Both sets of axes are right-handed systems and the equilibrium configurations of the CH_3 groups, even to the order of the numbering of the H atoms, are identically situated with regard to their own sets of axes. The z' and z'' axes are collinear but point in opposite directions along the symmetry axis of the molecule. The position of the z' axis is given by the polar angle θ and the equatorial angle φ; the orientation of the x', y' and x'', y'' axes is given by the azimuthal angles χ' and χ'', respectively, both being measured in the same direction from the same base line in the plane perpendicular to the z' axis. Thus, when $\gamma=0$ (see below), the x' and x'' axes are parallel and the y' and y'' axes are antiparallel. Two other coordinates are defined: $\gamma=(\chi'-\chi'')/2$, the internal angle; and $\chi=(\chi'+\chi'')/2$, which is used to help define a third system of axes x, y, z which is coincident with the x', y', z' system when $\gamma=0$. The positive x axis always bisects the angle between the x' and x'' axes and the z axis is always coincident with the z' axis. (See Fig. 1.)

The displacements of the ith atom relative to the x', y', z' (x'', y'', z'') axes are measured along the Cartesian axes ξ'_i, η'_i, ζ'_i (ξ''_i, η''_i, ζ''_i) which have their origin at the equilibrium positions of the ith atom and which are oriented parallel to the x', y', z' (x'', y'', z'') axes. The position chosen for the equilibrium configuration of a CH_3 group is suggested by Fig. 2.

Point Group

Regardless of the magnitude of the forces restricting internal rotation, it is evident that for an arbitrary value of the internal angle, the potential energy of a displacement of C_2H_6 from its equilibrium configuration will be unchanged by a reflection of the molecule in a plane perpendicular to the threefold symmetry axis. The transformation, in terms of the internal angle and the displacement coordinates, corresponding to this operation is

$$\gamma\rightarrow-\gamma,\quad \zeta'\leftrightarrow\xi'',\quad \eta'\leftrightarrow-\eta'',\quad \zeta'\leftrightarrow\zeta'',\quad 1'\leftrightarrow1'',\quad 2'\leftrightarrow3'',\quad 3'\leftrightarrow2'' \qquad (1)$$

(see Figs. 1 and 2; under the reflection the internal angle behaves as a vector directed along the threefold axis). The abstract group under

[2] Teller and Topley, J. Chem. Soc. 885 (1935).

which the potential energy of C_2H_6, with any sort of restriction on the internal motion, is invariant is thus D_{3h}, i.e., the direct product group formed from D_3 and the group of order two consisting of the identity operation and the reflection in a plane perpendicular to the threefold axis. Only when $\gamma=0$, however, does the above transformation (1) reduce to the transformation which describes a reflection of the displacement coordinates alone and which is a point group transformation for a rigid C_2H_6 molecule having a plane of symmetry perpendicular to the threefold axis. Because of this distinction in the transformations which describe the reflection we shall designate as D'_{3h} the point group of C_2H_6 with an arbitrary value of the internal angle[3] to distinguish the present more general case from that of a rigid symmetrical C_2H_6 molecule with point group D_{3h}. The derivation given by Teller and Topley[2] of the selection rules for C_2H_6 with free internal rotation makes use of the invariance of the potential energy under only the operations of the point group D_3. The point group D_3, whereas it describes the symmetry of the molecule in the ordinary sense, i.e., gives the complete set of independent physical operations which transform the *equilibrium* configuration of the molecule into a physically *indistinguishable* configuration, does not take full cognizance of the operations under which the potential energy is invariant, i.e., the operations which transform a *displaced* configuration of the molecule into a physically *equivalent* configuration. In other words, the point group D_3, although it describes the symmetry of the molecule, does not fully describe the symmetry of the normal modes of vibration.

By virtue of the transformation (1) the displacement coordinates form the basis for a representation of the group D'_{3h}. By standard methods[4] for reducing the representation we find that the fully reduced representation is[5]

$$\Gamma=3A_1+A_2+\bar{A}_1+3\bar{A}_2+4E+4\bar{E}.$$

Symmetry Coordinates

Our next step is to find a set of coordinates having the symmetry properties revealed in the last section. The normal coordinates are defined by the transformation

$$\xi'_i=\sum_k l'_{ik}Q_k,\quad \eta'_i=\sum_k m'_{ik}Q_k,\quad \zeta'_i=\sum_k n'_{ik}Q_k \qquad (2)$$

with similar expressions in l''_{ik}, m''_{ik}, n''_{ik} for ξ''_i, η''_i, ζ''_i.

We shall find it convenient in obtaining the normal coordinates to make use of two other special systems of coordinates. Let one set of coordinates Z'_m (Z''_m), referring to a single CH_3 group, be given by the transformation

$$\xi'_i=\sum_m \lambda_{im}Z'_m,\quad \eta'_i=\sum_m \mu_{im}Z'_m,\quad \zeta'_i=\sum_m \nu_{im}Z'_m. \qquad (3)$$

The transformation from ξ''_i, η''_i, ζ''_i to Z''_m is given by an *identical* set of coefficients λ_{im}, μ_{im}, ν_{im}. The summation over m extends from 1 to $3N/2$ where $N/2$ is the number of atoms in the CH_3 group. Furthermore, it shall be required that the coordinates Z'_m are normalized to $\frac{1}{2}$ and are orthogonal, that they form the basis for a fully reduced representation of the point group C_{3v} of the CH_3 group and that six of them are given by

$$\begin{aligned}
(Z'_{1a})Z'_\xi &= N_T\sum\sqrt{m_i}\xi'_i;\\
(Z'_{1b})Z'_\eta &= N_T\sum\sqrt{m_i}\eta'_i;\\
(Z'_1)Z'_\zeta &= N_T\sum\sqrt{m_i}\zeta'_i;\\
(Z'_{2b})Z'_{M\xi} &= N_R\sum\sqrt{m_i}(-c_i\eta'_i+b_i\zeta'_i);\\
(-Z'_{2a})Z'_{M\eta} &= N_R\sum\sqrt{m_i}(-a_i\zeta'_i+c_i\xi'_i);\\
(Z'_2)Z'_{M\zeta} &= N_R\sum\sqrt{m_i}(-b_i\xi'_i+a_i\eta'_i).
\end{aligned} \qquad (4)$$

The alternative notation for Z'_m given in parentheses may be ignored for the moment. N_T and N_R are normalization factors; m_i is the mass of the ith atom; a_i, b_i, c_i give the equilibrium values of x'_i, y'_i, z'_i for the ith atom; $\bar{c}_i$ is the z' coordinate of the equilibrium position of the ith atom as measured from the center of gravity of the singly-primed CH_3 group but with the positive direction of the z' axis unchanged.

If we let D denote the representation of the point group C_{3v} formed by the ξ'_i, η'_i, ζ'_i coordinates, then we may denote the reduction of D effected by the transformation to the Z'_m coordinates as the direct sum $D=3a_1+a_2+4e$.[6] We shall designate the three coordinates belonging to the

[3] We may equally well have made use of the invariance of the potential of C_2H_6, with an arbitrary restriction on internal rotation, under a reflection in the center of gravity of the molecule. We would then have built up a point group D'_{3d} whose operations are described by transformations which reduce to those of D_{3d} when $\gamma=\pi/2$. The transformation (1) does not reduce to the operation of inversion of D_{3d} when $\gamma=\pi/2$ and the molecule has a center of symmetry because the former transformation involves a reorientation of the x, y axes with respect to the molecule.

[4] E. Wigner, Gött. Nach. 133 (1930).

[5] The notation used is based on that of Mulliken, Phys. Rev. **43**, 279 (1933). We have used bars where he uses primes (e.g., $\bar{A}_1$, instead of A''_1) for his representations of the group D_{3h}.

[6] In the notation of Mulliken (reference 5) the a_1, a_2, e representations are A_1, A_2, E, respectively.

irreducible representation a_1 by $m=1, 2, 3$, the coordinate belonging to a_2 by $m=4$, and the pairs of coordinates belonging to the degenerate representation e by $m=5, 6, 7, 8$. Among the last type of coordinates we shall distinguish by the additional subscripts a and b the members of a pair of coordinates belonging to the two-dimensional e representation, and shall require that all the coordinates Z'_{ma} have identical transformation properties under operations of the group and that all Z'_{mb} have identical transformation properties. Choosing Z'_ξ and Z'_η as Z'_{5a} and Z'_{5b}, respectively, we thereby determine that Z'_{ma} and Z'_{mb} shall be, respectively, symmetric and antisymmetric with respect to reflection through the x', z' plane (see Fig. 2). Denoting $Z'_{M\xi}$ by Z'_{6b} we see that $Z'_{M\eta}$ corresponds to $-Z'_{6a}$ in order that Z'_{6a} be related to Z'_{6b} as Z'_{5a} is to Z'_{5b}. It is readily verified that $Z'_\xi=Z'_1$ belongs to a_1 and $Z'_{M\xi}=Z'_4$ is the coordinate belonging to a_2.

The second set of coordinates is given by the following linear combinations of the Z'_m and Z''_m coordinates:

$$S_m=Z'_m+Z''_m, \quad m=1, 2, 3, 4, \tag{5a}$$

$$\bar{S}_m=Z'_m-Z''_m, \quad \bar{m}=1, 2, 3, 4, \tag{5b}$$

$$S_{m\alpha}=(Z'_{ma}+Z''_{ma})\cos\gamma-(Z'_{mb}+Z''_{mb})\sin\gamma, \quad m=5, 6, 7, 8, \tag{5c}$$

$$\left.\begin{aligned}
S_{m\beta}&=(Z'_{ma}-Z''_{ma})\sin\gamma+(Z'_{mb}-Z''_{mb})\cos\gamma,\\
\bar{S}_{m\alpha}&=(Z'_{ma}+Z''_{ma})\sin\gamma+(Z'_{mb}+Z''_{mb})\cos\gamma,\\
\bar{S}_{m\beta}&=-(Z'_{ma}-Z''_{ma})\cos\gamma+(Z'_{mb}-Z''_{mb})\sin\gamma,
\end{aligned}\right\}\ \bar{m}=7, 8,$$

$$\begin{aligned}
\bar{S}_{5\alpha}&=(1+d^2)^{-\frac{1}{2}}\{[(Z'_{6a}+Z''_{6a})\sin\gamma+(Z'_{6b}+Z''_{6b})\cos\gamma]\\
&\quad+d[(Z'_{5a}+Z''_{5a})\sin\gamma+(Z'_{5b}+Z''_{5b})\cos\gamma]\},\\
\bar{S}_{5\beta}&=(1+d^2)^{-\frac{1}{2}}\{[-(Z'_{6a}-Z''_{6a})\cos\gamma+(Z'_{6b}-Z''_{6b})\sin\gamma]\\
&\quad+d[-(Z'_{5a}-Z''_{5a})\cos\gamma+(Z'_{5b}-Z''_{5b})\sin\gamma]\},
\end{aligned} \tag{5d}$$

$$\begin{aligned}
\bar{S}_{6\alpha}&=(1+d^2)^{-\frac{1}{2}}\{d[(Z'_{6a}+Z''_{6a})\sin\gamma+(Z'_{6b}+Z''_{6b})\cos\gamma]\\
&\quad-[(Z'_{5a}+Z''_{5a})\sin\gamma+(Z'_{5b}+Z''_{5b})\cos\gamma]\},\\
\bar{S}_{6\beta}&=(1+d^2)^{-\frac{1}{2}}\{d[-(Z'_{6a}-Z''_{6a})\cos\gamma+(Z'_{6b}-Z''_{6b})\sin\gamma]\\
&\quad-[-(Z'_{5a}-Z''_{5a})\cos\gamma+(Z'_{5b}-Z''_{5b})\sin\gamma]\},
\end{aligned}$$

where $d=N_R c_0/N_T$ and c_0 is the distance between the centers of gravity of the CH_3 group and the molecule as a whole in the equilibrium configuration. The subscripts α, β differentiate the members of a pair of coordinates belonging to a two-dimensional representation.

It may readily be verified that the S coordinates have the transformation properties required by the considerations of the preceding section.[7] The coordinates with $m=1, 2, 3, 4$ belong to the A_1 and A_2 irreducible representations of D'_{3h}, those with $\bar{m}=1, 2, 3, 4$ to $\bar{A}_1$ and $\bar{A}_2$, those with $m=5, 6, 7, 8$ to E and those with $\bar{m}=5, 6, 7, 8$ to $\bar{E}$. The physical nature of these coordinates is suggested by the diagrams of Fig. 2 in the paper of Stitt and Yost.[8]

The number of S coordinates is $3N$ whereas the number of degrees of vibrational freedom is $3N-7$. In II it is shown that by setting identically equal to zero certain linear combinations of the displacement coordinates, ξ'_i, η'_i, etc., which correspond to incipient translations, over-all rotations and internal rotation of the molecule, the vibrational and rotational kinetic energies can be separated to a first approximation.[9] Comparing the expressions in question (Eqs. (21) of II) with the S coordinates, we note the following identities:

$$\bar{S}_1=Q_z, \quad S_4=Q_{M\gamma}, \quad \bar{S}_4=Q_{Mz}, \quad S_{5\alpha}=Q_x,$$
$$S_{5\beta}=Q_y, \quad \bar{S}_{5\alpha}=Q_{Mx}, \quad \bar{S}_{5\beta}=Q_{My}$$

where the Q's are the Wigner[4] normal coordinates of over-all rotation, translation and internal rotation, relative to the x, y, z axes. By making these seven S coordinates identically zero we completely define our system of displacement coordinates. We shall call the remaining seventeen coordinates symmetry coordinates.[10] They form the following representation of D'_{3h}: $\Gamma=3A_1+2\bar{A}_2+3E+3\bar{E}$. The normal coordinate of internal rotation $Q_{M\gamma}$ belongs to the representation $\bar{A}_1$.

Normal Coordinates

The seventeen normal coordinates defined by the transformation (2) have the same transformation properties as the symmetry coordinates and the normal coordinates belonging to

[7] In performing the symmetry operations it is convenient to note that the transformation (1) has the following effect: $Z'_m \leftrightarrow Z''_m$ for nondegenerate coordinates; $Z'_{ma} \leftrightarrow Z''_{ma}$, $Z'_{mb} \leftrightarrow -Z''_{mb}$ for degenerate coordinates; $\gamma \to -\gamma$. It may be objected that inasmuch as the coefficients of the transformation from the displacement coordinates ξ'_i, η'_i, etc., to the S coordinates are not all constant under the operations of the group D'_{3h}, the standard methods of reducing the representation formed by the displacement coordinates do not apply. By setting $\gamma=0$, however, in the expressions (5) for the S coordinates, we have a set of coordinates which are obtained from the original displacement coordinates by a transformation with constant coefficients and which fully reduce the representation. The further transformation involving γ does not change the number of coordinates belonging to each irreducible representation of D'_{3h}.

[8] F. Stitt and D. M. Yost, J. Chem. Phys. **5**, 90 (1937). We are indebted to Dr. Stitt for allowing us to see the manuscript of his paper before publication. He has pointed out to us two errors in his diagrams. In $\delta(\sigma)$ of XY_3 an arrow has been omitted and in $\nu_6(\sigma)$ of X_2Y_6 an arrow points in the wrong direction.

[9] See reference 4; also C. Eckart, Phys. Rev. **47**, 552 (1935) and Wilson and Howard, J. Chem. Phys. **4**, 260 (1936).

[10] Howard and Wilson, J. Chem. Phys. **2**, 630 (1934).

a certain irreducible representation will be formed out of orthogonal linear combinations of the symmetry coordinates of that representation. If the transformation from the symmetry coordinates to the normal coordinates does not involve γ the dependence of both sets of coordinates on γ will consequently be of the same nature. The transformation in question depends on γ only if the coefficients in the potential energy expressed in terms of the symmetry coordinates are functions of γ. We shall show in the following section that in the case of free internal rotation these coefficients are independent of γ. Consequently, we may, by virtue of Eqs. (5), write the coefficients of the transformation (2) to the normal coordinates for the case of free internal rotation in the following way, allowing s'_{ik} to denote l'_{ik}, m'_{ik} or n'_{ik} and s''_{ik} to denote l''_{ik}, m''_{ik} or n''_{ik},

$$s'_{ik}=s_{ik};\quad s''_{ik}=s_{ik},\qquad k=1,2,3, \tag{6a}$$

$$s'_{ik}=s_{ik};\quad s''_{ik}=-s_{ik},\qquad k=4,5, \tag{6b}$$

$$\begin{aligned}
s'_{ik\alpha}&=s_{ik\alpha}\cos\gamma-s_{ik\beta}\sin\gamma,\\
s'_{ik\beta}&=s_{ik\alpha}\sin\gamma+s_{ik\beta}\cos\gamma,\\
s''_{ik\alpha}&=s_{ik\alpha}\cos\gamma-s_{ik\beta}\sin\gamma,\\
s''_{ik\beta}&=-s_{ik\alpha}\sin\gamma-s_{ik\beta}\cos\gamma,
\end{aligned}\qquad k=6,7,8, \tag{6c}$$

$$\begin{aligned}
\bar{s}'_{ik\alpha}&=\bar{s}_{ik\alpha}\sin\gamma+\bar{s}_{ik\beta}\cos\gamma,\\
\bar{s}'_{ik\beta}&=-\bar{s}_{ik\alpha}\cos\gamma+\bar{s}_{ik\beta}\sin\gamma,\\
\bar{s}''_{ik\alpha}&=\bar{s}_{ik\alpha}\sin\gamma+\bar{s}_{ik\beta}\cos\gamma,\\
\bar{s}'_{ik\beta}&=\bar{s}_{ik\alpha}\cos\gamma-\bar{s}_{ik\beta}\sin\gamma.
\end{aligned}\qquad \bar{k}=9,10,11, \tag{6d}$$

The unprimed coefficients s_{ik}, $s_{ik\alpha}$, $s_{ik\beta}$ are constants and show the relation between the singly and doubly primed coefficients. The numbering used above has been discarded but the distinction between the coordinates of the two types E and $\bar{E}$ is still made by using k and $\bar{k}$ to denote coordinates of different types. The above coefficients will be used in II in evaluating the kinetic energy.

Potential Energy

In terms of the symmetry coordinates, Eqs. (5), the most general quadratic potential function may be expressed as $V=\frac{1}{2}\sum C_{mn}(\gamma)S_mS_n+\Phi(\gamma)$. The force constants C_{mn} are functions of γ, and Φ is the potential energy governing the internal rotation of the equilibrium framework. The only assumptions underlying this expression are that the equilibrium positions of the atoms do not change as γ changes and that for all values of γ the vibrations are of infinitesimal amplitude. Since the potential energy is invariant under the operations of the point group D_3, which do not involve γ, there will be no cross terms between S_m's of the A_1 and $\bar{A}_2$ types or between either of these and the degenerate type. The question arises as to whether there are cross terms between the E and $\bar{E}$ coordinates. An investigation of the degenerate coordinates, Eqs. (5c, d), reveals that when one or more are excited, an internal rotation by $\pm 2\pi/6$ produces a vibration configuration physically equivalent to the initial configuration. Consequently, $C_{mn}(\gamma)$ must be such that if we expand it in a Fourier series about the position $\gamma=0$

$$C_{mn}=A^0{}_{mn}+A'_{mn}\cos 6\gamma+A''_{mn}\cos 12\gamma+\cdots \tag{7a}$$

or

$$C_{mn}=B'_{mn}\sin 6\gamma+B''_{mn}\sin 12\gamma+\cdots. \tag{7b}$$

Since under the reflection (1), $S_m\rightarrow+S_m$ or $-S_m$ according as S_m belongs to the E or $\bar{E}$ type, whereas the potential energy must be invariant, it is clear that between degenerate coordinates of the same type C_{mn} has the form (7a) and between degenerate coordinates of different types C_{mn} has the form (7b). The coefficients C_{mn} of the nondegenerate coordinates will have the form (7a).

Case of free internal rotation[11]

If there is no interaction between H atoms of different groups and consequently no cross

[11] We shall speak of a molecule as having free internal rotation if the molecule in its *equilibrium* configuration undergoes internal rotation without a change in potential energy. If a change in potential energy is involved the molecule will be said to have restricted internal rotation; if the potential is of such magnitude that the internal motion is for practical purposes entirely a torsional vibration, the internal rotation will be said to be completely restricted. This conception of free internal rotation, which seems to be the common one and implies the absence of direct forces between H atoms in different CH_3 groups, does not necessarily imply that the classical vibration frequencies are independent of the internal angle. Although the latter is found to be true in the case of C_2H_6 with free internal rotation, molecules in which the rotating parts are not symmetrical tops will have vibrations whose reduced

terms between the displacement of such atoms in the potential function, it can be shown by direct substitution of the expressions (5) for the S coordinates in the potential energy that the coefficients of the symmetry coordinates in the resulting expression do not involve the internal angle γ. Although the interaction energy of a C atom of one group with the atoms of the other group depends upon the projection of the displacements of the former onto the coordinate system of the latter and thus depends upon γ, this explicit appearance of γ is removed when the symmetry coordinates are introduced.

The normal coordinates for free internal rotation will thus have the same dependence on γ as do the symmetry coordinates, Eqs. (5). The normal vibrations for any value of the internal angle will be the same as for a molecule restricted to an internal torsion-vibration about that value of the angle.[12] In the nondegenerate vibrations the motion of the atoms of a CH_3 group with reference to the rotating axis system (x', y', z' or x'', y'', z'') of that group does not change as the molecule undergoes internal rotation. With the degenerate vibrations, however, it is otherwise. In these the two C atoms, which move in parallel or antiparallel directions, continue to move in the same direction relative to the x, y axes (see Fig. 1b), despite the relative motion of the two CH_3 groups.[13] Furthermore, if we hold a degenerate normal coordinate at a fixed non-zero value and vary the internal angle, the displaced H atoms in the groups will pulsate with the frequency of internal rotation, preserving at each moment translational and rotational momenta of the molecule as a whole. A characteristic difference between the E and $\bar{E}$ vibrations is that in the former the C atoms move in parallel directions, in the latter they move in antiparallel directions.

masses contain the internal angles (L. S. Kassel, J. Chem. Phys. **3**, 326 (1935)). Even though in this case there is, dynamically speaking, never actually free internal rotation, even in the ground vibrational state, it seems to us that it will avoid confusion if we retain the initial meaning of the term free internal rotation.

[12] The normal mode $Q_{M\gamma}$ is the sole representative of the $\bar{A}_1$ representation and hence cannot mix with any of the other normal modes.

[13] The motion of the two C atoms in the same direction makes the frequency of vibration independent of the internal angle. The symmetry coordinates $S_{6\alpha}$, $S_{6\beta}$, $\bar{S}_{6\alpha}$, $\bar{S}_{6\beta}$, Eq. (5), necessarily entail this sort of motion since otherwise the vibration would give rise to an over-all translation or rotation. In the remaining symmetry coordinates of the degenerate type, translation and rotation are conserved by the CH_3 groups separately. Nevertheless, only when $S_{6\alpha}$, $S_{6\beta}$, $\bar{S}_{6\alpha}$, $\bar{S}_{6\beta}$ are correct *normal* coordinates and when we can neglect the difference in energy between motions of the C atoms in parallel and antiparallel directions, in which case corresponding E and $\bar{E}$ vibrations become accidentally degenerate, is it permissible for the C atoms to move in independent directions in a normal vibration. The proper vibrations for the lifting of the fourfold E, $\bar{E}$ degeneracy are those in which the C atoms move in parallel and antiparallel directions. Only the former of these motions involves a resultant electric moment.

Case of restricted internal rotation

When interaction terms between H atoms of different CH_3 groups are introduced the potential energy coefficients of symmetry coordinates belonging to the same irreducible representation of D'_{3h} become of the form (7a). Let us imagine that we have chosen a set of coordinates Q^0_k such that $2V^0=\sum A^0_{mn}S_mS_n=\sum\lambda_k(Q^0_k)^2$. If the potential restricting internal rotation is small we may treat $V'=(1/2)\cos 6\gamma\sum A'_{mn}S_mS_n=(1/2)\cos 6\gamma\sum\lambda'_{kl}Q^0_kQ^0_l$ as a perturbation. The most important terms in the perturbation will be the squared terms, since the fundamental frequencies of vibrations of the same symmetry are widely separated. The restricting potential $\Phi(\gamma)$ may be represented by $B\cos 6\gamma$. Consequently, choosing an arbitrary vibrational state specified by the vibrational quantum numbers n_k, we may express the perturbation as one in γ alone, namely, as

$$V=\cos 6\gamma\{(1/2)\sum\lambda'_{kk}[(Q^0_k)^2]_{nknk}+B\}$$
$$=B'\cos 6\gamma, \quad (8)$$

in which $[(Q^0_k)^2]_{nknk}$ is the average value of $(Q^0_k)^2$ in the vibrational state n_k. The problem of calculating the energy levels of the internal motion for a given vibrational state is thus reduced to the same problem as that for the case of rigid CH_3 groups.[14] A calculation in which it is assumed that the forces between H atoms in different groups are repulsive and can be represented by a fraction[15] of a Morse potential function shows that the value of $\sum\lambda'_{kk}[(Q^0_k)^2]_{nknk}$ with all n_k's equal to zero is less than 10 percent of the value of B. The percentage is independent of the fraction of the Morse curve chosen. The

[14] See Nielsen, Phys. Rev. **40**, 445 (1932).

[15] This is the assumption made by Eyring, J. Am. Chem. Soc. **54**, 3191 (1932), and by Van Vleck and Cross, J. Chem. Phys. **1**, 357 (1933).

TABLE I. *Table of characters for the irreducible representations of the abstract group D'_{3h} and the distribution of the components of electric moment and polarizability and of the normal vibrations among the irreducible representations.*

D'_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	I.R.	R	ν
A_1	1	1	1	1	1	1		α_{zz}, $\alpha_{xx}+\alpha_{yy}$	$\nu_1\nu_2\nu_3$
A_2	1	1	−1	1	1	−1			
$\bar{A}_1$	1	1	1	−1	−1	−1			
$\bar{A}_2$	1	1	−1	−1	−1	1	μ_z		$\nu_4\nu_5$
E	2	−1	0	2	−1	0	μ_x, μ_y	$(-\alpha_{xx}+\alpha_{yy}, \alpha_{xy})$*	$\nu_6\nu_7\nu_8$
$\bar{E}$	2	−1	0	−2	1	0		α_{xz}, α_{yz}	$\nu_9\nu_{10}\nu_{11}$

* Consult the text.

energy levels of the internal motion are discussed further in II.

There is also a perturbation potential of the form

$$V' = (1/2)\sin 6\gamma \sum B'_{mn} S_m \bar{S}_n = (1/2)\sin 6\gamma \sum \lambda_{kl} Q^0{}_k \bar{Q}^0{}_l \quad (9)$$

between E and $\bar{E}$ coordinates which is important only when the E and $\bar{E}$ vibrations are almost degenerate.

Selection Rules

In deriving the selection rules we shall assume that the electric moment and the polarizability of each CH_3 group depend only on the coordinates of that group and that the electric moment and the polarizability of the molecule are the sums of the moments and polarizabilities of the two groups. It is convenient to focus one's attention on the x, y, z system of axes since it is found that the components of electric moment relative to these axes involve only the normal coordinates and not the internal angle, and that the same is true with two exceptions in the case of the components of the polarizability tensor.

Table I shows the essential facts regarding the vibrational transitions in the infrared and Raman spectra for the case of *free internal rotation*. The column under I.R. contains the allocation of μ_x, μ_y, μ_z the components of electric moment, to the irreducible representations of D'_{3h}. Thus $\bar{A}_2$ vibrations will give rise to parallel type bands and E vibrations to perpendicular type bands in the infrared.[16] In the column R is the corresponding distribution of the components of the polarizability tensor relative to the x, y, z axes among the representations, indicating that the A_1, E and $\bar{E}$ vibrations are Raman active. An unusual feature is presented by the components of the polarizability which fall into the E representation. The situation may be represented as follows if we expand polarizability components in terms of the normal coordinates and retain only the linear terms:

$$-\alpha_{xx}+\alpha_{yy} = \cos 3\gamma \sum \tau_k Q_{k\alpha} + \sin 3\gamma \sum \bar{\tau}_k \bar{Q}_{k\alpha},$$
$$2\alpha_{xy} = \cos 3\gamma \sum \tau_k Q_{k\beta} + \sin 3\gamma \sum \bar{\tau}_k \bar{Q}_{k\beta}. \quad (10)$$

In the last column of Table I the distribution of the normal vibrations among the representations is given in terms of the frequencies.

When a potential restricting internal rotation is introduced the vibrational selection rules remain unaltered except for the Raman activity of the E vibrations in the limit of complete restriction. This exception arises through the appearance of γ in the polarizability components of Eq. (10). If, in the limit of complete restriction of the internal rotation, $\gamma = 0$, $\pi/3$ or $2\pi/3$ and the molecule has a plane of symmetry perpendicular to the C−C axis, the E vibrations are active; they alone contribute to the components (10). If, on the other hand, $\gamma = \pi/6$, $\pi/2$ or $5\pi/6$ and the molecule has a center of symmetry, the E vibrations are inactive in the Raman spectrum since only the $\bar{E}$ vibrations contribute to the polarizability. The selection rules for the internal motion are discussed in the subsequent paper. Since the frequencies of the degenerate vibrations do not actually appear in the Raman spectrum, probably because of too low intensity, the Raman vibrational spectrum offers no clue as to whether there is small or large restriction of internal rotation.

The statement that the vibrational selection rules remain unaltered with the exception just discussed requires amplification inasmuch as the perturbation (9), which appears only when there are forces restricting the internal rotation, would seem to couple E and $\bar{E}$ vibrations. The coupling, however, involves the eigenfunctions for the internal rotation and transitions to $\bar{E}$ vibrations from the ground vibrational state may occur only when accompanied by changes in the quantum

[16] Teller and Topley (reference 2) on the basis of the selection rules for a molecule with point group D_3, which does not sufficiently describe the symmetry of the normal vibrations, concluded that all degenerate frequencies were active in the infrared.

number of the internal rotation. Further discussion of this point is postponed until II. It is concluded there that the infrared vibrational spectrum also offers no conclusive evidence regarding internal rotation.

Fundamental Frequencies

There is a twofold purpose in attempting to apply a normal coordinate treatment with a simple potential function to such a complex molecule as C_2H_6. One of these is to determine an approximate set of normal coordinates with which the vibrational angular momenta may be estimated; these quantities have an important use in II. The other purpose is to compute a set of vibration frequencies which may serve as a guide in the interpretation of regions of the vibrational spectrum where assignments of frequencies are uncertain.

To calculate the vibrational frequencies we have chosen the following valence-force-type potential function, which is equally well suited to free and restricted internal rotation,

$$2V=K_1\sum_i(\Delta r'^2_i+\Delta r''^2_i)+K_2r_0^2\{\sum_{i>j}(\Delta\alpha'^2_{ij}+\Delta\alpha''^2_{ij})+\sum_i(\Delta\beta'^2_i+\Delta\beta''^2_i)\}+K_3\Delta R^2. \quad (11)$$

The single and double primes refer to different CH_3 groups and i, j refer to the three H atoms of a group. K_1, K_2, K_3 are force constants; $\Delta r'_i$ is the change in the $C'-H'_i$ bond distance, $\Delta\alpha'_{ij}$ is the change in $H'_i-C'-H'_j$ bond angle, ΔR is the change in the $C'-C''$ bond distance, $\Delta\beta'_i$ is the change in the $H'_i-C'-C''$ bond angle; r_0 is the equilibrium value of the $C'-H'$ bond distance. It is to be noted that the force constants for the distortion of all bond angles are assumed to be the same, an assumption which can, perhaps, be justified only by the agreement with observed frequencies to which it leads. It is also assumed that the tetrahedral angles are preserved in CH_3.

Following are the equations giving the frequencies of vibration in terms of the force constants of (11). The equation for the three A_1 frequencies ν_1, ν_2, ν_3 is

$$\omega^3-\omega^2(K_1D+K'_2E+K'_3)+\omega(K_1K'_2F+K_1K'_3+K'_2K'_3)-K_1K'_2K'_3=0, \quad (12)$$

where $\omega=4\pi^2m\nu^2$, $D=(3m\tau^2/M)+1$,

$E=(3m\mu^2/M)+1$, $F=(3m/M)+1$,

$K'_3=(2m/M)K_3$, $K'_2=(Z+1)K_2$,

$Z=12\tau^2/(4-3\mu^2)$;

m and M are the masses of the H and C atoms, respectively; $\mu=\sin\beta^0$ and $\tau=\cos\beta^0$ where β^0 is the equilibrium value of the bond angle $H'-C'-C''$. The equation for the $\bar{A}_2$ frequencies ν_4, ν_5 may be obtained from Eq. (12) by letting $K'_3=0$. The E frequencies ν_6, ν_7, ν_8 are the roots of the equation

$$\omega^3-\omega^2\{K_1L/2+K''_2Q/2+K_2[2(F+1)+G\tau^2]/2L\}+\omega\{K_1K''_2N+K_1K_2(F+1)/2+K''_2K_2[4F+G(1+\tau^2)]/2L\}-K_1K''_2K_2F=0, \quad (13)$$

where $L=E+1$, $Q=[(3m\mu^2/M)-2]\mu^2+4$,

$G=(3m\mu/M)^2$, $N=L-\mu^2$, $K''_2=3K_2/(4-3\mu^2)$

and the other quantities are given above. The equation for the $\bar{E}$ frequencies ν_9, ν_{10}, ν_{11} is too complicated to be reproduced here.

Table II gives the results of the calculation. The "calculated" frequencies enclosed in paren-

Table II. *Observed and calculated frequencies in cm^{-1} and force constants in dynes/cm for C_2H_6. The observed frequencies were obtained from the following sources: Infrared (gas),[17] Raman (gas),[18] Raman (gas),[19] Raman (liq.).[20]*

	Obs.		Calc.			Obs.		Calc.	
ν_1	993	R	(993)	R	ν_6	827	I.R.	840	I.R.
ν_2	1460 (liq.)		1570 2910		ν_7	1480		1480	(R.)
ν_3	2927*				ν_8	3000		3020	
ν_4	1380	I.R.	(1380)	I.R.	ν_9	—		1005	R
ν_5	2926†		(2900)		ν_{10}	—		1515	
					ν_{11}	—		3025	

$K_1=4.79\times10^5$, $K_2=0.46\times10^5$, $K_3=5.62\times10^5$

* $\nu_2=2927$ cm^{-1} is the mean of the two Raman frequencies 2899 cm^{-1} and 2955 cm^{-1}.

† $\nu_5=2926$ cm^{-1} is the mean of the two infrared frequencies 2896 cm^{-1} and 2955 cm^{-1}.

[17] Levin and Meyer, J. Opt. Soc. Am. **16**, 137 (1928).
[18] Lewis and Houston, Phys. Rev. **44**, 903 (1933).
[19] Bhagavantam, Ind. J. Phys. **6**, 595 (1932).
[20] Daure, Ann. de physique **12**, 375 (1929).

theses were used to evaluate K_1, K_2, K_3. The other frequencies calculated with the values of the force constants so obtained agree surprisingly well with the remaining eight observed frequencies except for ν_2, the calculated value of which is 8 percent higher than the shift of 1460 cm^{-1} observed in the Raman spectrum[20] of liquid C_2H_6. We assign this strong Raman line tentatively to ν_2 following Sutherland and Dennison.[1] The pair of Raman frequencies 2899 and 2955 cm^{-1} probably arises from resonance between ν_3 and $2\nu_7$ in close analogy to the resonance proposed by Barker and Adel[21] for the methyl halides. The overtone corresponding to $2\nu_{10}$ likewise has an A_1 component which could resonate with ν_3 but, lacking other evidence, we shall have to assume there is sufficient difference between the values of $2\nu_7$ and $2\nu_{10}$ to explain the appearance of two rather than three Raman lines. Similarly the pair of infrared frequencies 2896 and 2955 cm^{-1} probably arises from resonance between ν_5 and $\nu_7+\nu_{10}$. The ν_7 and ν_{10} and also the ν_8 and ν_{11} vibrations are very similar except for a phase difference of π in the vibrations of one CH_3 group, and the vibration corresponding to $\nu_7+\nu_{10}$ has an $\bar{A}_2$ component which may resonate with ν_5. The correctness of the first interpretation could be tested by polarization measurements on the pair of Raman lines in question. It is possible that the weak Raman line of frequency 975 cm^{-1} found by Bhagavantam[19] corresponds to ν_9. Kemp and Pitzer[22] have found that the heat capacity of C_2H_6 in the range 140 to 400°K is well reproduced with statistical-mechanical calculations based upon a restricting potential of about 3150 cal. and a value of 1160 cm^{-1} for ν_9.

[21] Adel and Barker, J. Chem. Phys. **2**, 627 (1934).

[22] We wish to thank Doctors Kemp and Pitzer for permitting us to see a copy of their paper on the entropy of C_2H_6 before publication.

In the infrared rotation-vibration spectrum obtained by Levin and Meyer[17] there is scarcely more evidence for two perpendicular type bands in the ν_7 (1480) region, differing by about 30 cm^{-1}, than in the very similar band of CH_3F. The same may be said of the band corresponding to $\nu_8=3000$ cm^{-1}. Yet Bartholomé and Sachsse,[23] using less resolving power, which revealed only the band envelopes, found distinct evidence of two bands of approximately equal intensity at 1465 and 1495 cm^{-1}. We have seen that through the perturbation (9) there may be a coupling of E and $\bar{E}$ vibrations whereby the latter may become active in the infrared, but the selection rules governing the appearance of the $\bar{E}$ vibrations involve a change in the quantum number of the internal rotation (or torsion oscillation). A further discussion of this point is deferred to *II* where it is concluded that the second band found by Bartholomé and Sachsse cannot be satisfactorily explained as a fundamental $\bar{E}$ frequency.

Conclusion

The fundamental region of the vibrational Raman and infrared spectra of C_2H_6 is satisfactorily accounted for with the selection rules of the point group D'_{3h} and the frequencies calculated with a three-constant valence-force type of potential function, without knowledge of the magnitude of the restriction of the internal rotation, except for a doubtful point introduced by the two infrared bands found by Bartholomé and Sachsse in the 1480 cm^{-1} region. This point is discussed in the subsequent paper along with additional evidence bearing on the magnitude of the potential between CH_3 groups.

[23] Bartholomé and Sachsse, Zeits. f. physik. Chemie **B30**, 40 (1935).

The Rotation-Vibration Spectrum of C_2H_6 and the Question of Free Internal Rotation

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If there were *free* internal rotation in C_2H_6 the rotational structure of certain perpendicular type infrared bands would be very different from that for the customary symmetrical top molecule without internal rotation. To account for the fact that this difference is not observed it is necessary to assume that there is a potential difference of *at least* 2000 cal. (700 cm^{-1}) between the two symmetrical forms of C_2H_6 differing by an internal rotation of $2\pi/6$. A potential of this magnitude corresponds to an internal torsion vibration of 230 cm^{-1}. The above conclusion is based upon a dynamical treatment of C_2H_6 in which it is assumed that vibration, over-all rotation, and internal rotation subject to a restricting potential may occur simultaneously. An approximate form of the Hamiltonian expression obtained is $\mathbf{H} = \frac{1}{2}\{(\mathbf{P}_x - \mathbf{p}_x)^2/A + (\mathbf{P}_y - \mathbf{p}_y)^2/A + (\mathbf{P}_z - \mathbf{p}_z)^2/C + (\mathbf{P}_\gamma - \mathbf{p}_\gamma)^2/C + \sum \mathbf{p}_k^2\} + V$, where γ represents the angle of internal rotation. The rotational selection rules are determined and it is found that under ordinary circumstances the internal rotation when free is inactive in the infrared rotation-vibration spectrum. However, when there is *accidental* degeneracy of certain pairs of twofold degenerate vibrational levels, the internal rotation becomes active in the infrared bands for these vibrations. In such a case of accidental vibrational degeneracy, which is approximated to by at least two sets of vibrations in C_2H_6, the rotation-vibration frequency for the infrared bands involves the quantity $(h/4\pi^2)[(K \pm K')(1-\zeta)/C - K/A]$ if the internal rotation is free; K and K' are the quantum numbers of over-all and internal rotation about the threefold symmetry axis and ζ is a quantity depending on the angular momentum of vibration. The observed rotational spacing, however, is well reproduced by a frequency containing instead the quantity $(h/4\pi^2)K[(1-\zeta)/C - 1/A]$, which is to be expected if C_2H_6 is an ordinary symmetrical top molecule without internal rotation.

INTRODUCTION

THE study of the infrared bands of C_2H_6 presented below affords strong evidence for the presence of a potential of at least 2000 cal. restricting internal rotation. Kemp and Pitzer[1] have also found from statistical mechanical calculations that with a potential of about 3000 cal. they can explain the results of various experiments on the entropy and specific heat of C_2H_6, and the heat of reaction and the equilibrium constant for the $C_2H_4+H_2=C_2H_6$ reaction. It should be pointed out that Smith and Vaughan[2] in discussing the discrepancy between their statistical mechanical calculation of the equilibrium constant based on the heat of hydrogenation of C_2H_4 and the assumption of almost free internal rotation of C_2H_6 concluded that the principal source of uncertainty lay in the analysis of the problem of free internal rotation. In contrast to these results stands the theoretical value of about 360 cal. calculated by Eyring[3] for the restricting potential; the configuration of highest potential energy is that in which there is a plane of symmetry perpendicular to the C–C axis. The contribution of the vibrational zero-point energy to such a potential is negligible according to the results of the preceding paper. The only remaining terms which may contribute to the potential are of the type suggested by Penney[4] in his considerations of the electronic energy of C_2H_6. In the method of molecular orbitals these terms arise from the integrals involving the overlapping of the orbitals of a C atom and the orbitals of the H atoms of one CH_3 group together with the distances to the H atoms of the other group. An estimate of the effect of such terms on the restricting potential has not yet been made but their contribution to the potential must far outweigh the other contributions if the discrepancy between the theoretical value for the magnitude of the potential and the values determined from thermodynamic and spectroscopic data is to be removed.

GENERAL CONSIDERATIONS

Before proceeding to the mathematical treatment of the rotation-vibration energy of C_2H_6, we shall present, from a slightly different viewpoint from that adopted in the main body of the paper, the essential ideas which lead one to

* Society of Fellows, Harvard University.
[1] Kemp and Pitzer, J. Chem. Phys. **4**, 749 (1936).
[2] Smith and Vaughan, J. Chem. Phys. **3**, 341 (1935).
[3] Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).
[4] W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934).

conclude that there cannot be free internal rotation in C_2H_6. There are two types of degenerate vibrations in C_2H_6, one in which the C atoms move in parallel directions while the two CH_3 groups rotate relative to one another about the symmetry axis, and one in which the C atoms move in antiparallel directions. The former type is active in the infrared, the latter inactive. In both types of vibration the internal rotation is inactive since the electric moments of the CH_3 groups perpendicular to the symmetry axis do not take part in the internal rotation; the relative motion of the C atoms is the same when the CH_3 groups are rotating and when they are not. In a special case of accidental degeneracy of vibrations of different types, however, the electric moments can be regarded as fixed in the CH_3 groups, whereupon the internal rotation becomes active in the infrared. We shall consider an ideal situation which is approximately realized separately by the ν_7 (1480) and ν_{10} (1515) and the ν_8 (3020) and ν_{11} (3025) sets of vibrations as the work of the preceding paper shows. Let us assume that in these degenerate vibrations, angular momentum and translational momentum are conserved in each CH_3 group separately, and that the accidental degeneracy of vibrations of different types is complete (i.e., $\nu_7=\nu_{10}$ and $\nu_8=\nu_{11}$). The latter signifies that the frequency of vibration is independent of whether the C atoms move in parallel or antiparallel directions. Consequently, in the resulting fourfold degenerate vibrational level it is possible to construct vibrations in which the direction of the electric moment produced in one CH_3 group is independent of the relative orientation of the other CH_3 group.[5] This situation has been discussed by Nielsen;[6] the selection rules for K and K', the quantum numbers of over-all and internal rotation about the symmetry axis, respectively, are $\Delta K=\pm 1$, $\Delta K'=\pm 1$, the changes being independent of one another. The rotation-vibration frequency corresponding to the zero branches ($\Delta J=0$) in the infrared band resulting from a transition from the ground vibrational state to the fourfold degenerate vibrational level is thus

$$\nu_{KK'}=\nu_v-(h/8\pi^2)(2/C-1/A)\pm(h/4\pi^2)[(K\pm K')/C-K/A],$$

where ν_v is the vibrational frequency and the sign combinations are four in number. When the coupling of rotation and vibration is taken into consideration the fourfold vibrational degeneracy is lifted and the expression for the frequency becomes

$$\nu_{KK'}=\nu_v-(h/8\pi^2)(2/C-1/A)\pm(h/4\pi^2)[(K\pm K')(1-\zeta)/C-K/A],$$

where ζ is a quantity which is determined by vibrational angular momentum directed along the symmetry axis of the molecule. The rotational structure of the infrared band corresponding to this expression consists of a series of lines of spacing $(h/4\pi^2)[2(1-\zeta)/C-1/A]$ about each of which appears a second series of spacing $(h/4\pi^2)1/A$. The rotational structure actually observed in the C_2H_6 spectrum is that of a single series of lines with a spacing corresponding to $\Delta\nu=(h/4\pi^2)[(1-\zeta)/C-1/A]$, which is the spacing to be expected if C_2H_6 is an ordinary symmetrical top without internal rotation. The magnitude of the restricting potential which is necessary in order that a distortion of the rotational structure of the ν_7 and ν_8 bands by internal rotation would probably just escape observation is about 2000 cal. (700 cm^{-1}).

Approximate Hamiltonian Expression[7]

In the appendix of this paper it is shown that the approximate form of the Hamiltonian of C_2H_6 corresponding to the form used by Johnston and Dennison[8] for symmetrical and spherical top molecules is

$$\mathbf{H}=\tfrac{1}{2}\{(\mathbf{P}_x-\mathbf{p}_x)^2/A+(\mathbf{P}_y-\mathbf{p}_y)^2/A+(\mathbf{P}_z-\mathbf{p}_z)^2/C+(\mathbf{P}_\gamma-\mathbf{p}_\gamma)^2/C+\sum\mathbf{p}_k^2\}+V. \quad (1)$$

The notation and coordinate system used is fully explained in the appendix and in the preceding paper,[9] and the following explanations will suffice here. A and C are equilibrium moments of inertia of C_2H_6 about axes perpendicular to and

[5] See footnote 13 of the preceding paper.
[6] Nielsen, Phys. Rev. **40**, 445 (1932).
[7] The present study is related to that of Nielsen (reference 6) in the following way. Nielsen developed the dynamical theory of a rigid symmetrical top the two halves of which may undergo a constrained relative rotation about the axis of symmetry. The model of C_2H_6 studied here is one in which vibration may occur as the molecule undergoes internal and over-all rotation.
[8] Johnston and Dennison, Phys. Rev. **48**, 868 (1935).
[9] The preceding paper will henceforth be referred to as I.

collinear with the symmetry axis, respectively; $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$ are the components of the total overall angular momentum (see Eqs. (30) in appendix) and $\mathbf{p}_x$, $\mathbf{p}_y$, $\mathbf{p}_z$ are the corresponding components of the vibrational angular momentum (Eqs. (34)); $\mathbf{p}_k$ is the momentum conjugate to the kth normal coordinate, Q_k (Eq. (32)). V is the potential energy.

Special notice should be taken of the fact that $\mathbf{P}_\gamma$ and $\mathbf{p}_\gamma$ do not correspond to the total internal angular momentum and the vibrational internal angular momentum. Their expressions, to the approximation with which we are dealing, are (see Eqs. (31), (34))

$$P_\gamma = C\dot{\gamma} + \sum_k (\mathfrak{Z}'_k + \mathfrak{Z}''_k)\dot{Q}_k + \sum_k \Delta_k \dot{Q}_k, \quad (2)$$

$$p_\gamma = \sum_k (\mathfrak{Z}'_k + \mathfrak{Z}''_k)\dot{Q}_k + \sum_k \Delta_k \dot{Q}_k, \quad (3)$$

where $\mathfrak{Z}'_k$, $\mathfrak{Z}''_k$ and Δ_k are given in Eqs. (25), (27), (28). The last term $\sum \Delta_k \dot{Q}_k$ which is common to both expressions distinguishes P_γ and p_γ from the total and vibrational internal angular momenta, respectively. It has its origin in the fact that when a degenerate vibration is excited the kinetic energy relative to the rotating axis systems of the individual CH_3 groups depends upon the velocity of internal rotation, in other words, the normal coordinates for the degenerate vibrations contain the internal angle implicitly. The additional term arises only through the interaction of two degenerate vibrations of different symmetry types (i.e., E and $\bar{E}$ vibrations).

Energy Matrix

Case of free internal rotation

In setting up the energy matrix for the Hamiltonian operator (1), it is convenient to use a set of wave functions ψ° which diagonalize the Hamiltonian

$$\mathbf{H}^\circ = \tfrac{1}{2}\{\mathbf{P}_x^2/A + \mathbf{P}_y^2/A + \mathbf{P}_z^2/C + \mathbf{P}_\gamma^2/C + \sum \mathbf{p}_k^2 + \sum \lambda_k Q_k^2\}. \quad (4)$$

The remaining terms

$$\mathbf{H}' = -\{\mathbf{P}_x\mathbf{p}_x/A + \mathbf{P}_y\mathbf{p}_y/A + \mathbf{P}_z\mathbf{p}_z/C + \mathbf{P}_\gamma\mathbf{p}_\gamma/C\} \quad (5)$$

may be considered as a perturbation. We have neglected squares of the vibrational angular momentum since their contribution to the vibrational energy is negligible. It is evident from the expressions for $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$ in Eq. (30) that the first three terms of Eq. (4) are identical with the Hamiltonian of a rigid symmetrical top. We may therefore, for the case of free internal rotation, write the wave functions[6] which diagonalize $\mathbf{H}^\circ$ (except for a normalization factor) as

$$\psi^\circ = \Theta_{JKM}(\vartheta) e^{iM\varphi} e^{iK\chi} e^{iK'\gamma} \psi_v(Q)$$
$$M, K = -J, -J+1 \cdots +J, \quad (6)$$

where $\Theta_{JKM} e^{iM\varphi} e^{iK\chi}$ is the wave function for a symmetrical top and J is the total quantum number. ψ_v is the vibrational wave function involving Hermitean polynomials.

In order that ψ° be single valued it must remain unchanged under the transformation $\chi' \to \chi' + 2\pi$ or $\chi'' \to \chi'' + 2\pi$, each of which restores the molecule to its initial configuration if the displacements of the atoms relative to the equilibrium framework are held fixed. The transformations of the angles are equivalent to $\chi \to \chi + \pi$, $\gamma \to \gamma \pm \pi$. The interesting feature in this connection is that the normal coordinates transform differently under the operation in question. From Eqs. (5) of I it is seen that when $\gamma \to \gamma \pm \pi$ and the displacements of the atoms are held fixed $Q \to Q$ if the normal coordinate is nondegenerate and $Q \to -Q$ if the normal coordinate is degenerate. Consequently, under the operation, $\psi_{ve} \to \psi_{ve}$ if the number of quanta in excited degenerate vibrations is even and $\psi_{vo} \to -\psi_{vo}$ if this number is odd. These cases will be designated as V_e and V_o, respectively. Furthermore, $e^{iK\chi} \to (-1)^K e^{iK\chi}$ and $e^{iK'\gamma} \to (-1)^{K'} e^{iK'\gamma}$ under the transformation. Consequently, given a value of K it is evident that the choice of K' is limited by the fact that the following equations must be satisfied: $(-1)^{K+K'} = 1$ in the V_e case and $(-1)^{K+K'+1} = 1$ in the V_o case. It is evident that the following wave functions meet these requirements of single valuedness

$$\left.\begin{aligned} \psi_e^\circ &= \Theta_{JKM}(\vartheta) e^{iM\varphi} e^{iK\chi} e^{i(2S+K)\gamma} \psi_{ve} \\ \psi_o^\circ &= \Theta_{JKM}(\vartheta) e^{iM\varphi} e^{iK\chi} e^{i(2S+K+1)\gamma} \psi_{vo} \end{aligned}\right\}$$
$$S = 0, \pm 1, \pm 2 \cdots. \quad (7)$$

With these wave functions it is possible to

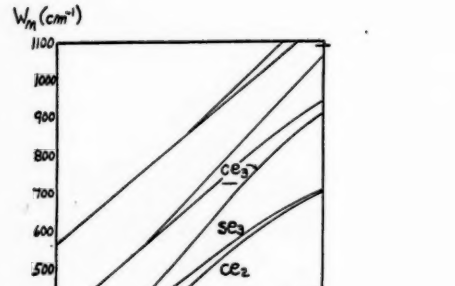

FIG. 1. Diagram of certain energy levels as functions of q and $2B$ for internal rotation in C_2H_6, and related eigenfunctions $ce_0(x)$, $se_1(x)$, etc., where $x=3\gamma$.

write down the energy matrix corresponding to the operator $\mathbf{H}^\circ+\mathbf{H}'$. The eigenvalues of $\mathbf{H}^\circ$ are evidently

$$W=(h^2/8\pi^2)\{J(J+1)/A+K^2(1/C-1/A)+K'^2/C\}+W_v, \quad (8)$$

where K' is given by $2S+K$ and $2S+K+1$ in the V_e and V_o cases, respectively, and W_v is the vibrational energy. If we let R, R' and V, V' denote two sets of rotational quantum numbers and two sets of vibrational quantum numbers, respectively, a typical element of the perturbation matrix $\mathbf{H}'$ may be written

$$(H')_{RV;\,R'V'}=-\sum_\alpha (P_\alpha)_{R;\,R'}(p_\alpha)_{V;\,V'}/I_\alpha, \quad (9)$$

where $\alpha=x, y, z, \gamma$ and $I_x=I_y=A$, $I_z=I_\gamma=C$.

Case of restricted internal rotation

The portion of the Schrödinger wave equation of the molecule which depends on the internal angle may be written

$$[(\mathbf{P}_\gamma-\mathbf{p}_\gamma)^2/2C+B\cos 6\gamma]\psi(\gamma)=W_\gamma\psi(\gamma). \quad (10)$$

In this expression it is assumed that the potential energy between CH_3 groups may be expressed in the form $B\cos 6\gamma$. In I it was shown that this form of the potential is not changed even if we include the dependence of the normal vibrations on the internal angle.

Let us break the expanded Hamiltonian of (10) into

$$\mathbf{H}_\gamma^\circ=\mathbf{P}_\gamma^2/2C+B\cos 6\gamma \quad (11)$$

and a perturbation Hamiltonian

$$\mathbf{H}'_\gamma=-\mathbf{P}_\gamma\mathbf{p}_\gamma/C+\mathbf{p}_\gamma^2/2C. \quad (12)$$

The wave functions and energy levels as functions of B for the equation $\mathbf{H}_\gamma^\circ\psi(\gamma)=W_\gamma^\circ\psi(\gamma)$ have been discussed by Nielsen, who considered the equation as a special form of the Mathieu equation

$$y''(x)+(a-16q\cos 2x)y(x)=0, \quad (13)$$

where

$$x=3\gamma,\ a=(8\pi^2C/9h^2)W_\gamma^\circ \text{ and } 16q=(8\pi^2C/9h^2)B.$$

The latter equation has been studied extensively by Goldstein,[10] among others.

In Fig. 1 is reproduced a diagram of the energy levels corresponding to Eq. (13) for different values of q. We have omitted for the sake of simplicity the energy levels for values of K' which are not multiples of 3. The omitted levels, doubly degenerate when $q=0$, retain their degeneracy when q becomes finite and do not cross the other levels. When $q=0$ the eigenfunctions $ce_n(x)$ and $se_n(x)$ (in the notation of Goldstein) reduce, except for a constant factor, to $\cos 3n\gamma$ and $\sin 3n\gamma$, respectively. The correlation of wave functions and energy levels given in the diagram is for $q>0$, which corresponds to a molecule in which the configuration of lowest potential energy has a center of symmetry. When $q<0$ and the configuration of lowest potential energy has a plane of symmetry perpendicular to the C–C axis, the same diagram obtains but the proper wave functions are obtained by making the substitution $\gamma=\gamma+\pi/6$, i.e., $x=x+\pi/2$.

SELECTION RULES

It was explained in I that if the components of the electric moment μ and the polarizability tensor α are referred to the x, y, z axes carried by the molecule (see Fig. 1b of I) the components then involve only the normal coordinates, with two exceptions in which the internal angle

[10] S. Goldstein, Trans. Camb. Phil. Soc. **23**, 303 (1927).

appears as follows:

$$-\alpha_{xx}+\alpha_{yy}=\cos 3\gamma\sum\tau_k Q_{k\alpha}+\sin 3\gamma\sum\bar{\tau}_k\bar{Q}_{k\alpha},$$
$$2\alpha_{xy}=\cos 3\gamma\sum\tau_k Q_{k\beta}+\sin 3\gamma\sum\bar{\tau}_k\bar{Q}_{k\beta}. \quad (14)$$

Inasmuch as the part of the nuclear wave functions depending on θ, φ, χ and determining the motion of the x, y; z system of axes are identical with rigid symmetrical top wave functions, and since electric moment and polarizability can be referred to the x, y, z axes without employing θ, φ, χ, the selection rules for J, K, M will be identical with those for a rigid symmetrical top. The internal rotation will be inactive in the infrared spectrum except in the case of accidental degeneracy of an E and an $\bar{E}$ vibration as discussed below. It will also be inactive in the Raman spectrum with the exceptional case arising because of the appearance of γ in the expressions (14); the selection rules corresponding to these components of the polarizability, which involve E and $\bar{E}$ normal vibrations, are $\Delta K=\pm 3$. It is to be noted that the selection rules for K and K' are compatible with the values of the quantum number K' allowed by boundary conditions, Eq. (7).

When a potential restricting the internal rotation is applied, only those vibrational transitions, with one exception, are permitted in which the state of the internal motion is the same in the initial and final states of the transition, since the internal angle does not enter in the electric moment and polarizability. The exception once again concerns the polarizability components (14). In these components the E vibrations have as coefficient $\cos 3\gamma$, typical matrix elements of which occur between states connected by the dotted vertical lines of Fig. 1. The $\bar{E}$ vibrations have as coefficient $\sin 3\gamma$, typical matrix elements of which are represented by the dot-dash vertical lines of Fig. 1. Thus, in the limit $q=\infty$, $-\alpha_{xx}+\alpha_{yy}$ and $2\alpha_{xy}$ may be expanded in terms of states involving E vibrations plus odd multiples of the normal coordinate of internal torsion vibration $Q_{M\gamma}$ and in terms of $\bar{E}$ vibrations plus even multiples of $Q_{M\gamma}$. The limit $q=\infty$ in the case represented by Fig. 1 corresponds to a molecule with a center of symmetry. When $q<0$, the situation is reversed. The dotted lines represent matrix elements of $\sin 3\gamma$ and the dot-dash lines elements of $\cos 3\gamma$, so that in the limit $q=-\infty$, the E vibrations are associated with even multiples of $Q_{M\gamma}$ and the $\bar{E}$ vibrations with odd multiples in the expansion of $-\alpha_{xx}+\alpha_{yy}$ and $2\alpha_{xy}$. This case corresponds to a molecule with a plane of symmetry. These selection rules for the internal motion when $|q|=\infty$ are identical, as they should be, with the selection rules derived for a molecule in which the internal motion is regarded as a normal coordinate vibration.

Rotational Structure of Infrared Bands

P_zp_z coupling

The effect of introducing the z coupling term in $\mathbf{H}'$, Eqs. (5), (9), will be the same as in the case of a symmetrical top without internal rotation. This coupling is of greatest importance in the case of a pair of degenerate vibrations. The rotational spacing in the infrared perpendicular type band arising from degenerate vibrations has been fully discussed by Johnston and Dennison.[8] We shall give only the expression for the rotational spacing: $\Delta\nu=(h/4\pi^2)[(1-\zeta)/C-1/A]$. The z component of the angular momentum of vibration in the pair of vibrational states resulting from the rotation-vibration coupling is given by $p_z=\pm\zeta h/2\pi$; ζ is a positive or negative quantity according as the sense of rotation of the electric moment and the direction of the angular momentum of vibration are parallel or antiparallel. Transitions from the ground state to a degenerate-type vibration occur with $\Delta K=+1$ or -1 according as the vibration is such that the $+$ or $-$ sign appears before ζ in the expression for p_z. With the use of the normal coordinates obtained in I the quantity ζ has been computed for the three perpendicular-type bands from the expression for p_z given in Eqs. (34), (24), (25) of the appendix. The comparison of the observed and calculated[11] rotational spacings is shown in

TABLE I. *Rotational spacing in cm^{-1} of perpendicular type infrared bands of C_2H_6.*

ν	ζ	$\Delta\nu_{obs}$	$\Delta\nu_{calc}$
ν_6 (827)	0.218	2.6	2.63
ν_7 (1480)	−0.368	4.9	5.60
ν_8 (3000)	0.150	3.3	2.98

[11] The values used for the moments of inertia were $C=10.94\times10^{-40}$ g cm^2 and $A=41.88\times10^{-40}$ g cm^2. All

Table I. The agreement is surprisingly good in view of the simplicity of the normal coordinate treatment given. In the absence of rotation-vibration coupling we would expect a rotational spacing $\Delta\nu=3.74$ cm^{-1}. It can be shown that the sum of the ζ's for the three E vibrations is $\sum\zeta_k=0$, so that the sum of the calculated rotational spacings for the corresponding infrared bands should be three times the normal spacing, i.e., $3\times3.74=11.22$ cm^{-1}.

$\mathbf{P}_\gamma\mathbf{p}_\gamma$ coupling

If the matter of rotation-vibration coupling ended at this point the agreement between the observed and calculated rotational spacing would be gratifying. The matrix elements of $\mathbf{p}_\gamma$ connecting E and $\bar{E}$ vibrations, however, may be quite appreciable and in view of the approximate degeneracy[12] of ν_7 (1480) and ν_{10} (1515) and of ν_8 (3020) and ν_{11} (3025), the coupling terms in Eq. (12) must be considered. It is not difficult to obtain the effect of the coupling on the appearance of an infrared band in the case discussed at the beginning of the paper, namely where there is complete degeneracy of an E and an $\bar{E}$ vibration and where there is complete freedom of internal rotation. As a result of the rotation-vibration coupling, Eq. (12), the fourfold degenerate vibrational state, for a given value of K and K', is split into four components which are characterized by the four possible different combinations of signs in the expressions $\mathbf{p}_s=\pm\zeta h/2\pi$ and $\mathbf{p}_\gamma=\pm\rho h/2\pi$. In such a case the expression for the rotation-vibration frequency, corresponding to the zero branches ($J\rightarrow J$) of the perpendicular type band, assumes a particularly simple form, namely,

$$\nu_{KK'}=\nu_V-(h/8\pi^2)\{(1-\rho^2)/C-1/A\}$$
$$\pm(h/4\pi^2)\{K[(1-\zeta)/C-1/A]\mp K'\rho/C\}, \quad (15)$$

where the quantum numbers K and K' refer to the final state in the transition. Since the electric moment does not involve the internal angle, as it does χ, the duplicity in signs in $\mathbf{p}_\gamma$ appears in the frequency. In the special case of vibrational degeneracy which we are discussing, $\rho=\zeta-1$, so that the expression for the rotational frequency in the perpendicular type band assumes the form[13]

$$\nu_{KK'}=\nu_V-(h/8\pi^2)(2\zeta/C-1/A)$$
$$\pm(h/4\pi^2)\{(K\pm K')(1-\zeta)/C-K/A\} \quad (16)$$

if we neglect squares of ζ.

Whereas the E and $\bar{E}$ vibrations are not actually degenerate, the proximity of ν_7 and ν_{10} and of ν_8 and ν_{11} is enough to produce a marked effect of the $\mathbf{P}_\gamma\mathbf{p}_\gamma$ coupling on the rotational structure. The infrared band structures for C_2H_6 are not, however, discernibly different from those of such molecules as the methyl halides, which have no internal rotation. The fact that the secondary structure depending upon different values of K' is not observed can only mean that there is present a potential restricting internal rotation to such an extent that the internal angular momentum of *rotation* is quenched in all those levels of the internal motion which have an appreciable relative Boltzmann factor. By quenching of the internal angular momentum is meant that the matrix for $\mathbf{P}_\gamma$ is altered to such a degree that the perturbation $\mathbf{P}_\gamma\mathbf{p}_\gamma/C$ has an imperceptible effect on the energy.

In the following paragraphs we give the method used for making a quantitative estimate of a lower limit to the magnitude of the restricting potential $B\cos6\gamma$ below which the structure

bond angles were assumed to have the tetrahedral value and C was chosen as twice the moment of inertia of CH_4 as given by Johnston and Dennison (reference 8). To calculate A the following distances were assumed: C–C $=1.54A$ and C–H $=1.11A$. The former value was taken from Pauling and Huggins, Zeits. f. Krist. **A87**, 205 (1934), and the latter from Johnston and Dennison.

[12] The values given for the frequencies are those calculated in the preceding paper. Since the magnitudes of the ν_7, ν_{10} and ν_8, ν_{11} separations are important for what follows, a word may be said concerning them. If the forces between distant H atoms are neglected, ν_7 and ν_8 should be less than ν_{10} and ν_{11}, respectively, since in the former, the motion of the C atoms in parallel directions produces less change in potential energy than the antiparallel motion of the C atoms in the latter. A change of only a few cm^{-1} in the separations is produced by introducing a repulsion between distant H atoms which is represented by a fraction of a Morse potential and which gives 350 cal. for the potential restricting internal rotation.

[13] From the derivation of this expression it appears as if the term $K'(1-\zeta)/C$ arose purely out of the coupling of internal angular momentum and the vibrational angular momentum. However, even if the vibrational angular momentum is absent, i.e., $\zeta=0$, the contribution of the term $\mathbf{P}_\gamma\mathbf{p}_\gamma$ in the Hamiltonian does not vanish. This illustrates the fact mentioned above that $\mathbf{P}_\gamma$ and $\mathbf{p}_\gamma$ do not correspond simply to the total internal angular momentum and the internal vibrational angular momentum. The difference between expression (16) and that obtained for $\nu_{KK'}$ earlier is that in the present instance $K'=2S+K+1$ whereas in the earlier expression $K'=2S+K$.

TABLE II. *Relative displacements $\Delta\nu_n$ of frequencies in cm^{-1} due to the perturbation $P_\gamma p_\gamma/C$, relative energies W_n in cm^{-1} and relative Boltzmann factors at $T=300°K$ for the three lowest levels of the internal motion with $B=364$ cm^{-1}.*

$\nu_l-\bar{\nu}_l$	0	−20	−40	W_n	$e^{-W_n/kT}$
$\Delta\nu_0$	0	0	0	0	1.00
$\Delta\nu_1$	$-0.25\rho^2$	$0.24\rho^2$	$0.76\rho^2$	230	0.33
$\Delta\nu_2$	$3.68\rho^2$	$4.40\rho^2$	$5.25\rho^2$	430	0.13

$\rho_{7,10}=-1.37$;
$\rho_{8,11}=-0.85$

of the perpendicular type bands of C_2H_6 cease to resemble those of a molecule with completely restricted internal rotation.

For this purpose it is necessary to evaluate the matrix elements $-(P_\gamma)_{RR'}(p_\gamma)_{VV'}/C$ of the perturbation Hamiltonian (12). We shall confine our attention to the elements of p_γ connecting the almost degenerate vibrational states corresponding to ν_7 and ν_{10} and to ν_8 and ν_{11}. From the normal coordinates obtained for these vibrations in I and the expression (3) for p_γ we find that $\rho_{7,10}=-1.37h/2\pi$ and $\rho_{8,11}=-0.85h/2\pi$. Certain of the matrix elements of P_γ can be calculated using the solutions $ce_0(x)$, $se_2(x)$ and $ce_2(x)$ of the Mathieu equation (13) as obtained by Goldstein. Another pair of solutions $se_4(x)$ and $ce_4(x)$, which reduce to sin 12γ and cos 12γ (except for a constant factor) when $B=0$, have been obtained from the orthogonality relations with the above solutions. Solutions of higher energy, $se_6(x)$, $ce_6(x)$, etc., have been assumed to be well represented, within the range of values of B in which we are interested, by their values when $B=0$, namely sin 18γ, cos 18γ, etc. In Fig. 1 typical matrix elements of P_γ (for either of the cases $q>0$ and $q<0$) are represented by the solid vertical lines. Having obtained the matrix elements of P_γ connecting the states in question it is possible by a second-order perturbation treatment to evaluate the perturbation energy corresponding to $P_\gamma p_\gamma/C$ for the states $ce_0(x)$, $se_2(x)$ and $ce_2(x)$. When B is reasonably large these states become components of the three lowest levels of the internal torsion oscillation (see Fig. 1).

The perturbation treatment has been made for two magnitudes of the restricting potential, $B=182$ cm^{-1} and $B=364$ cm^{-1}. Table II gives the results of the calculation for the latter case. With such a value of B the three lowest energy levels closely correspond to an internal torsion vibration. In Table II $\Delta\nu_n$ represents the perturbation energy of the nth level minus that of the ground level, $n=0$. Consequently, $\Delta\nu_n$ gives the spacing of the secondary structure about each zero branch of the perpendicular type bands where n denotes the particular level of the internal motion which is involved in both the initial and final states of the transition. The energy of the nth level relative to the level $n=0$ is given under W_n in the table. In the last column of the table are given the relative Boltzmann factors of these levels at $T=300°K$. Below the table are given the values of ρ connecting the ν_7 and ν_{10} and the ν_8 and ν_{11} vibrations. To make the perturbation calculation it is necessary to know the separations $\nu_7-\nu_{10}$ and $\nu_8-\nu_{11}$. The values obtained in the preceding paper for these separations are -35 cm^{-1} and -5 cm^{-1}, respectively. Although the sign of these values is probably correct the magnitudes may be in error. Hence the calculation has been carried out for three values of the separation of the E and $\bar{E}$ frequencies, $\nu_l-\bar{\nu}_l=0$, -20 and -40 cm^{-1}.

From Table II we may conclude in the case of the perpendicular type bands corresponding to ν_7 (1480 cm^{-1}) and ν_8 (3020 cm^{-1}) that the effects of the coupling term $-P_\gamma p_\gamma/C$ are, respectively, as follows (we assume for explicitness that $\nu_{10}=1520$ cm^{-1} and $\nu_{11}=3020$ cm^{-1}): of the molecules in the three lowest levels of the internal torsion oscillation 9 percent give rise to lines displaced by 10 cm^{-1} and 2.7 cm^{-1} from the zero branches of the two bands and 23 percent give rise to lines which are displaced by 1.4 cm^{-1} and 0.2 cm^{-1}. This is the situation with $B=364$ cm^{-1}. With the lower value $B=182$ cm^{-1} the displacements are far greater. We would probably be justified in stating that the internal potential must be at least as high as 546 cm^{-1} since the C_2H_6 perpendicular type bands closely resemble those of an ordinary symmetrical top molecule but it was not thought worthwhile to repeat the perturbation calculations with this higher value of B. The value $2B=728$ cm^{-1} (2070 cal.) may be taken as a reasonable *lower* limit for the magnitude of the restricting potential. This value of the potential corresponds to an internal torsion frequency of 230 cm^{-1}; when $B=546$ cm^{-1} the torsion frequency is 300 cm^{-1}.

The above considerations concerning the coupling of E and $\bar{E}$ vibrations are complicated by the fact that there exists a second type of coupling between such vibrations (see Eq. (9) of I) which may arise when there are forces restricting internal rotation. The effect of this second type of coupling on the selection rules for the $\bar{E}$ vibrations is similar to that produced by the presence in the electric moment of such a term as $\sin 6\gamma\sum\bar{\tau}_k\bar{Q}_k$ where $\bar{Q}_k$ is an $\bar{E}$ vibration. Typical nonvanishing matrix elements of sin 6γ are represented by the solid vertical lines in Fig. 1. The frequency in the infrared spectrum associated with an $\bar{E}$ normal vibration will be the $\bar{E}$ fundamental frequency augmented or diminished by the energy difference of states of the internal motion connected by the solid

vertical lines. The resulting band would be very complex in the limit of small q whereas in the limit $q=\infty$ the active frequency would be $\bar{\nu}_k \pm \nu_\gamma$, where $\bar{\nu}_k$ is the $\bar{E}$ fundamental frequency and ν_γ is the frequency of the internal torsion oscillation. The two infrared bands found by Bartholomé and Sachsse[14] at 1465 and 1495 cm^{-1} cannot, however, be explained with any value of q. If q is large, then, since the E and $\bar{E}$ fundamental frequencies in this region, ν_7 and ν_{10}, are almost degenerate, the two bands should be separated by the frequency of the internal torsion oscillation, instead of by the small difference of 30 cm^{-1} calculated for the separation in the preceding paper. If q is small, say of such a magnitude that $2B=350$ cal., then instead of a single $\bar{E}$ frequency there should appear several frequencies separated from this by about 25 cm^{-1}, 50 cm^{-1}, 100 cm^{-1}, etc.

The presence of the second type of coupling between E and $\bar{E}$ vibrations represented by Eq. (9) of I does not seriously alter the conclusions reached concerning the $\mathbf{P}_\gamma \mathbf{p}_\gamma$ coupling of such states. The former coupling should be of the same order of magnitude as the similar coupling terms in Eq. (8) of I. The latter have been calculated and for a potential which gives a difference of 125 cm^{-1} (350 cal.) between the D_{3h} and D_{3d} configurations of C_2H_6 this type of coupling is less important than the rotation-vibration coupling. When the potential difference reaches 2000 cm^{-1} the former coupling may be of the same order of magnitude as the rotation-vibration coupling for the ν_7, ν_{10} pair but is still much less than the rotation-vibration coupling for the ν_8, ν_{11} pair.

$\mathbf{p}_x$, $\mathbf{p}_y$ coupling

Because of the symmetry relations involved, $\mathbf{p}_x$ and $\mathbf{p}_y$ may have matrix elements connecting only E with $\bar{E}$ or A_1 with $\bar{E}$ or $\bar{A}_2$ with E vibrations. In order for coupling to occur the vibrations so connected must be approximately degenerate. Fortunately, because of the similarity of those E and $\bar{E}$ vibrations which are quasidegenerate, the elements of $\mathbf{p}_x$ and $\mathbf{p}_y$ connecting them should be vanishingly small. The $\bar{A}_2$ vibrations are separated from the E vibrations by about 100 cm^{-1} and we should not expect coupling here, at least for the lower values of K', since it is found that $(p_x)_{lk}h^2/4\pi^2A$ is only equal to 0.066 cm^{-1} and 0.80 cm^{-1} for the ν_4, ν_7 and ν_5, ν_8 combinations, respectively, when internal rotation is free. Similarly ν_8 is separated by about 100 cm^{-1} from the combination bands of ν_2, ν_4 and of ν_7, ν_{10}. Consequently, we should not expect the structures of the infrared bands of the E vibrations to be seriously perturbed by coupling through $\mathbf{p}_x$, $\mathbf{p}_y$ with other vibrations.

In conclusion I would like to thank Professor E. Bright Wilson, Jr., for suggesting the problem of the ethane type molecule to me and for his invaluable advice during the course of this study.

Appendix: The Kinetic Energy of C_2H_ℓ

Classical kinetic energy

The method used to obtain the Hamiltonian form of the kinetic energy is very similar to that used by Wilson and Howard,[15] and we shall present here only the more important equations and expressions which appear in the derivation. Whereas the complete Hamiltonian expression has been derived, only the equations leading to the simplified form used in the present paper will be given. To obtain the simplified Hamiltonian from the complete expression one neglects linear and quadratic terms in the normal coordinates Q_k except for the terms in $Q_k\dot{Q}_k$ which appear in the vibrational angular momenta.

The kinetic energy T prior to the introduction of the normal coordinates is, to the approximation with which we are dealing,

$$\begin{aligned}2T=&A\omega_x^2+A\omega_y^2+C\omega_z^2+C\dot{\gamma}^2\\&+2(\omega_xM_x+\omega_yM_y+\omega_zM_z+\dot{\gamma}M_\gamma)\\&+\sum_i(\dot{\xi}'^2_i+\dot{\eta}'^2_i+\dot{\zeta}'^2_i)+\sum_i(\dot{\xi}''^2_i+\dot{\eta}''^2_i+\dot{\zeta}''^2_i),\end{aligned}\quad(17)$$

where A and C are the equilibrium moments of inertia of C_2H_6 about axes perpendicular to and collinear with the symmetry axis, respectively; ω_x, ω_y, ω_z are the components relative to the x, y, z axes (see Fig. 1 of I) of the angular velocity of these axes; $\dot{\gamma}$ is the time derivative of the internal angle. The expressions for the latter quantities in terms of the x', y', z' and x'', y'', z'' components of the vector angular velocities $\boldsymbol{\omega}'$ and $\boldsymbol{\omega}''$, respectively, of the primed sets of axes are

$$\begin{aligned}&\omega_x=(1/2)[(\omega'_x+\omega''_x)\cos\gamma-(\omega'_y+\omega''_y)\sin\gamma];\\&\omega_y=(1/2)[(\omega'_x-\omega''_x)\sin\gamma+(\omega'_y-\omega''_y)\cos\gamma];\\&\omega_z=(1/2)(\omega'_z-\omega''_z);\quad\dot{\gamma}=(1/2)(\omega'_z+\omega''_z).\end{aligned}\quad(18)$$

M_x, M_y, M_z are the x, y, z components of the vibrational angular momentum and M_γ is the internal angular momentum; they are given by the following expressions in

[14] Bartholomé and Sachsse, Zeits f. physik. Chemie **B30**, 40 (1935).

[15] Wilson and Howard, J. Chem. Phys. **4**, 260 (1936).

terms of the displacement coordinates (see Fig. 2 of I)

$$M_x=(M'_x+M''_x)\cos\gamma-(M'_y+M''_y)\sin\gamma;$$
$$M_y=(M'_x-M''_x)\sin\gamma+(M'_y-M''_y)\cos\gamma; \quad (19)$$
$$M_z=(M'_z-M''_z); \quad M_\gamma=(M'_z+M''_z).$$

where

$$M'_x=\sum(\eta'_i\dot\zeta'_i-\dot\eta'_i\zeta'_i); \quad M'_y=\sum(\zeta'_i\dot\xi'_i-\dot\zeta'_i\xi'_i);$$
$$M'_z=\sum(\xi'_i\dot\eta'_i-\dot\xi'_i\eta'_i) \quad (20)$$

and M''_x, M''_y, M''_z are given by similar expressions in ξ''_i, η''_i, ζ''_i.

The transformation (2) of I to the normal coordinates is next made. The displacement coordinates ξ'_i, η'_i, etc., are completely defined by the following seven conditions on the normal coordinates

$$Q_x=(Q'_x+Q''_x)\cos\gamma-(Q'_y+Q''_y)\sin\gamma=0;$$
$$Q_y=(Q'_x-Q''_x)\sin\gamma+(Q'_y-Q''_y)\cos\gamma=0;$$
$$Q_z=Q'_z-Q''_z=0;$$
$$Q_{Mx}=(Q'_{Mx}+Q''_{Mx})\cos\gamma-(Q'_{My}+Q''_{My})\sin\gamma=0; \quad (21)$$
$$Q_{My}=(Q'_{Mx}-Q''_{Mx})\sin\gamma+(Q'_{My}-Q''_{My})\cos\gamma=0;$$
$$Q_{Mz}=Q'_{Mz}-Q''_{Mz}; \quad Q_{M\gamma}=Q'_{Mz}+Q''_{Mz};$$

where

$$Q'_x=N_T\sum\sqrt{m_i}\xi'_i; \quad Q'_y=N_T\sum\sqrt{m_i}\eta'_i;$$
$$Q'_z=N_T\sum\sqrt{m_i}\zeta'_i; \quad Q'_{Mx}=N_R\sum\sqrt{m_i}(b_i\zeta'_i-c_i\eta'_i);$$
$$Q'_{My}=N_R\sum\sqrt{m_i}(c_i\xi'_i-a_i\zeta'_i);$$
$$Q'_{Mz}=N_R\sum\sqrt{m_i}(a_i\eta'_i-b_i\xi'_i), \quad (22)$$

with similar expressions in ξ''_i, η''_i, ζ''_i for Q''_x, Q''_y, Q''_z, Q''_{Mx}, Q''_{My}, Q''_{Mz}. N_T and N_R are normalization constants, a_i, b_i, c_i are the equilibrium values of x'_i, y'_i, z'_i (x''_i, y''_i, z''_i) for the ith atom, and m_i is the mass of the ith atom. To evaluate the terms which appear in the kinetic energy (17) we note that from Eq. (2) of *I*, $\dot\xi'_i=\sum l'_{ik}\dot Q_k+\sum\dot l'_{ik}Q_k$, etc., and that from Eq. (6) of *I*, $s'_{ik\alpha}=-s'_{ik\beta}\dot\gamma$, $s''_{ik\alpha}=s''_{ik\beta}\dot\gamma$, $s'_{ik\beta}=s'_{ik\alpha}\dot\gamma$, $s''_{ik\beta}=-s''_{ik\alpha}\dot\gamma$, where $s'_{ik\alpha}$, $s''_{ik\alpha}$, etc., represent the coefficients of the transformation (2) of *I* to the degenerate type normal coordinates. Using this information we have, from Eqs. (19), (20),

$$M_x=\sum\mathfrak{X}_k\dot Q_k; \quad M_y=\sum\mathfrak{Y}_k\dot Q_k;$$
$$M_z=\sum\mathfrak{Z}_k\dot Q_k; \quad M_\gamma=\sum\Gamma_k\dot Q_k; \quad (23)$$

where

$$\mathfrak{X}_k=(\mathfrak{X}'_k+\mathfrak{X}''_k)\cos\gamma-(\mathfrak{Y}'_k+\mathfrak{Y}''_k)\sin\gamma;$$
$$\mathfrak{Y}_k=(\mathfrak{X}'_k-\mathfrak{X}''_k)\sin\gamma+(\mathfrak{Y}'_k-\mathfrak{Y}''_k)\cos\gamma; \quad (24)$$
$$\mathfrak{Z}_k=(\mathfrak{Z}'_k-\mathfrak{Z}''_k); \quad \Gamma_k=(\mathfrak{Z}'_k+\mathfrak{Z}''_k),$$

and

$$\mathfrak{X}'_k=\sum_{il}(m'_{il}n'_{ik}-m'_{ik}n'_{il})Q_l;$$
$$\mathfrak{Y}'_k=\sum_{il}(n'_{il}l'_{ik}-n'_{ik}l'_{il})Q_l; \quad (25)$$
$$\mathfrak{Z}'_k=\sum_{il}(l'_{il}m'_{ik}-l'_{ik}m'_{il})Q_l.$$

Similarly,

$$\sum_i(\dot\xi'^2_i+\dot\eta'^2_i+\dot\zeta'^2_i)+\sum_i(\dot\xi''^2_i+\dot\eta''^2_i+\dot\zeta''^2_i)$$
$$=\sum_k\dot Q_k^2+2\dot\gamma\sum_k\dot Q_k\Delta_k, \quad (26)$$

where

$$\Delta_k=\Delta'_k+\Delta''_k;$$
$$\dot\gamma\Delta'_k=\sum_{il}(\dot l'_{il}l'_{ik}+\dot m'_{il}m'_{ik}+\dot n'_{il}n'_{ik})Q_l. \quad (27)$$

Δ_k is different from zero only between normal coordinates of different degenerate types (E and $\bar E$). Its nature is more completely revealed by the expression

$$\sum_k\Delta_k\dot Q_k=\sum_{kl}\Delta_{kala}\{\dot Q_{k\alpha}Q_{l\alpha}+\dot Q_{k\beta}Q_{l\beta}-Q_{k\alpha}\dot Q_{l\alpha}$$
$$-Q_{k\beta}\dot Q_{l\beta}\}, \quad (27a)$$

where k refers to an E coordinate and l to an $\bar E$ coordinate, and

$$\Delta_{kala}=\sum_i(l_{ika}l_{ila}+m_{ika}m_{ila}+n_{ika}n_{ila}). \quad (28)$$

The coefficients l_{ika}, l_{ila}, etc., correspond to the constant coefficients s_{ika}, s_{ila}, etc., of Eq. (6) of I and the summation is over all the atoms of the molecule.

Substituting the Eqs. (23), (26) into the kinetic energy (17) we obtain

$$2T=A\omega_x^2+A\omega_y^2+C\omega_z^2+C\dot\gamma^2+\sum_k\dot Q_k^2$$
$$+2\omega_x\sum_k\mathfrak{X}_k\dot Q_k+2\omega_y\sum\mathfrak{Y}_k\dot Q_k+2\omega_z\sum\mathfrak{Z}_k\dot Q_k$$
$$+2\dot\gamma\sum(\Gamma_k+\Delta_k)\dot Q_k. \quad (29)$$

Hamiltonian form

The next step is to obtain the Hamiltonian form of the kinetic energy. The components of the total angular momentum are given by

$$P_x=\partial T/\partial\omega_x=A\omega_x+\sum\mathfrak{X}_k\dot Q_k;$$
$$P_y=A\omega_y+\sum\mathfrak{Y}_k\dot Q_k; \quad P_z=C\omega_z+\sum\mathfrak{Z}_k\dot Q_k. \quad (30)$$

The momenta P_γ and p_k conjugate to γ and Q_k are

$$P_\gamma=\partial T/\partial\dot\gamma=C\dot\gamma+\sum(\Gamma_k+\Delta_k)\dot Q_k \quad (31)$$

and

$$p_k=\partial T/\partial\dot Q_k=\mathfrak{X}_k\omega_x+\mathfrak{Y}_k\omega_y+\mathfrak{Z}_k\omega_z+(\Gamma_k+\Delta_k)\dot\gamma+\dot Q_k. \quad (32)$$

P_γ is not identical with the total internal angular momentum given by $C\dot\gamma+\sum\Gamma_k\dot Q_k$. By means of Eqs. (30), (31), (32) the kinetic energy (29) may be rewritten

$$2T=(P_x-p_x)^2/A+(P_x-p_y)^2/A+(P_z-p_z)^2/C$$
$$+(P_\gamma-p_\gamma)^2/C+\sum_kp_k^2, \quad (33)$$

where

$$p_x=\sum\mathfrak{X}_kp_k, \quad p_y=\sum\mathfrak{Y}_kp_k,$$
$$p_z=\sum\mathfrak{Z}_kp_k, \quad p_\gamma=\sum(\Gamma_k+\Delta_k)p_k. \quad (34)$$

The transformation of the classical Hamiltonian expression into the corresponding Schrödinger equation in operator form has been discussed in reference 15. The momenta P_x, P_y, P_z are given by Eq. (30) of reference 15 in terms of the momenta conjugate to the Eulerian angles θ, φ, χ. The operators $\mathfrak{p}_\theta$, $\mathfrak{p}_\varphi$, $\mathfrak{p}_\chi$, $\mathfrak{p}_\gamma$, $\mathfrak{p}_k$ are obtained by replacing p_θ, p_φ, p_χ, p_γ, p_k by $h/2\pi i$ times $\partial/\partial\theta$, $\partial/\partial\varphi$, $\partial/\partial\chi$, $\partial/\partial\gamma$, $\partial/\partial Q_k$, respectively, in the classical expressions for the momenta. The quantum-mechanical analog of (33) is thus found to be identical in form with it but P_x, P_y, P_z, P_γ, p_x, p_y, p_z, p_γ, p_k are to be construed as operators.

The Structure of Caesium Nitrate

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STARTING with some investigations on the rotation of anions in cubic crystals we had the opportunity of studying the crystal structure of a series of nitrates including $CsNO_3$ in the temperature interval between room temperature and the melting point. The results of these investigations have been or will be published elsewhere, but a brief account on the caesium nitrate work is given in the present article because our results contradict those published in this journal by L. Waldbauer and D. C. McCann.[1]

Beside the x-ray investigation, an optical examination of the crystals in polarized light was carried out, and the correctness of the result of Gossner[2] and also Wallerant[3] definitely confirmed, $CsNO_3$ indeed being cubic between the transition point at 161° and the melting point. X-ray data of the cubic form of $CsNO_3$ have recently been published by the present authors in a paper dealing with cubic nitrates of monovalent cations.[4]

Single crystals of $CsNO_3$ are not destroyed when heated above the transition temperature (to 200°C) and then cooled down to room temperature. Rotation photographs of the same crystal taken (*a*) at room temperature (*b*) at 200°C and (*c*) after cooling back to room temperature are shown in Fig. 1.[5] From the reversible character of the transition of single crystals and the fact that diffraction patterns at ordinary temperature and at 200° are nearly identical (except for the weakening of the reflections at greater angles at 200°) the conclusion must be drawn that the positions of the Cs^+ ions are very little altered during the process of transition. The Cs^+ ion lattice in the high temperature form is a simple cubic one with a lattice constant of about 4.49A, and so we must assume it to be a pseudocubic lattice with ~4.45A in the low temperature form.

It seems extremely difficult to determine the true symmetry of the caesium nitrate crystals in the low temperature form. Apparently no reliable observations exist indicating a biaxial character of the crystals, but the close resemblance with rubidium nitrate crystals which are no doubt orthorhombic makes the assumption of hexagonal symmetry rather problematic. If this assumption is made, however, we are able to show that the most probable space group is C_{3v}^2. The only possible coordinates for the caesium ions having hexagonal symmetry and leading to the pseudocubic arrangement mention above are:

$$0\,0\,0 \quad \tfrac{1}{3}\,\tfrac{2}{3}\,0 \quad \tfrac{2}{3}\,\tfrac{1}{3}\,0 \quad x\,0\,z \quad 0\,x\,z \quad \bar{x}\,0\,\bar{z} \quad 0\,\bar{x}\,\bar{z} \quad x\,x\,\bar{z} \text{ and } \bar{x}\,\bar{x}\,z$$

x being nearly $\frac{1}{3}$ and z nearly $\frac{2}{3}$. Possible space groups are: C_3^1 C_{3i}^1 C_{3v}^2 D_3^1 and D_{3d}^1. The crystal classes C_{3i} and D_{3d} possessing both a center of symmetry must be rejected, however, because $CsNO_3$ crystals according to our observations are strongly pyroelectric (the same result was obtained with $RbNO_3$ crystals). A considerable number of $CsNO_3$ crystals was examined under the microscope, the development of crystal faces indicating that the class D_3 has to be excluded also. The distinction between the two remaining classes C_3 and C_{3v} is not so easily performed, but it seems at least very probable that under the condition in question the ditrigonal-pyramidal class is the right one and the space group of $CsNO_3$ C_{3v}^2. It is interesting to notice that our result refering to caesium nitrate is just the result to which Pauling and Sherman were led, though in a somewhat different way, in the case of rubidium nitrate.[6]

[1] L. Waldbauer and D. C. McCann, J. Chem. Phys. **2**, 615 (1934).
[2] Gossner, Zeits. f. Krist. **38**, 144 (1904).
[3] Wallerant, Bull. Soc. fr. min. **28**, 325 (1905).
[4] C. Finbak and O. Hassel, Zeits. f. physik. Chemie **B35**, 25 (1937).
[5] The photographs reproduced here are taken with Cu-radiation. Close to the incident beam, layer-lines due to the secondary emitted Cs *K* radiation may be observed. See Finbak and Hassel, Norsk. geol. Tidsskr. **16** (1936), Nature **139**, 194 (1937), Avh. Oet. Norske Vid. Akad. Oslo I Mat-natv. Kl. (1937) No. 2.
[6] Pauling and Sherman, Zeits. f. Krist. **84**, 213 (1933).

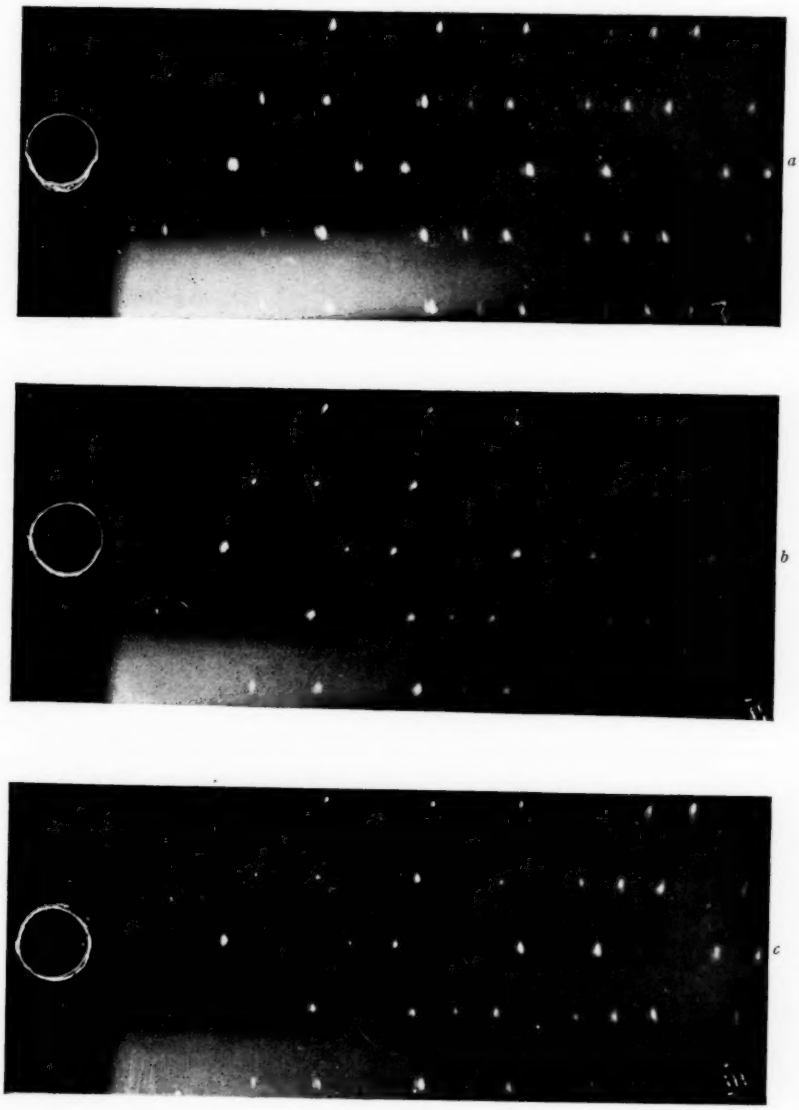

FIG. 1.

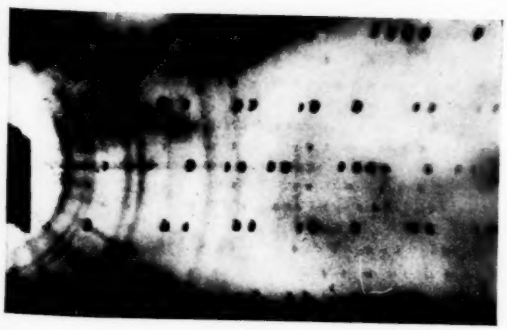

FIG. 2.

Fig. 2 shows part of a rotation photograph of $CsNO_3$, the orthohexagonal a axis being the axis of rotation. The weaker layer-lines indicate that the true period in the direction of this axis is not given by the period of the Cs^+ but is three times as large. In the paper of Waldbauer and McCann are to be found reproductions of powder photographs of CsCl, CsI, KIO_3 and $CsNO_3$. The apparently very high degree of resemblance between the photograph of CsI and $CsNO_3$ is rather misleading, however.

The Size of Nuclei in Solid Metal Reactions

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THE Tammann concept of the crystallization process as one taking place in two stages, (*a*) the formation of crystal nuclei, and (*b*) the subsequent growth of these nuclei, has met with general success in dealing with all crystallization phenomena.[1] The number of atoms required for the formation of such a nucleus has not been determined, but it will be shown in this paper that existing data provide a means of placing an upper limit upon this number for solid metal reactions.

Consider the formation of a new crystal B from its parent lattice A. In the simplest case of the recrystallization of a cold-worked pure metal, B may differ from A only in orientation. However, if an allotropic transformation in a pure metal is involved B will have a different lattice from that of A. The crystal B may also be a new phase precipitating from its solid solution in A, or may be formed by a eutectoid decomposition of A; in these cases it may differ from A in composition as well as in orientation and lattice type. Whatever the type of phase change, the general nature of the process is the same. The thermal vibration of the atoms will allow a number of them to form the lattice of B; such a cluster may either continue to grow as a new crystal or it may decompose again into A. Statistically speaking, when a cluster attains a certain size its tendency to grow will be greater than its tendency to decompose. It is this critical size, which may be called an effective nucleus, which we seek to limit.

The orientation relationships resulting from the formation of a new phase B from a matrix A have been determined for a wide variety of metal systems by Mehl and his co-workers.[2] A brief summary of these and other studies has been given by Sachs.[3] From this work it is evident that the orientation of B is always dependent upon that of A. Just what determines this orientation relationship is not yet completely understood, but the near matching of atomic positions on specific planes of the two phases is certainly a principal factor. In the series of papers by Mehl, it has been frequently pointed out that the orientation of B is probably determined by the small number of atoms which form its nucleus, and that atomic matching is not important in the subsequent growth of this nucleus. The same conclusion was reached by Sloat and Menzies[4] in a study of oriented overgrowths from salt solutions. That is, the orientation of the entire B crystal is determined by the orientation of the nucleus from which it grows, and this nucleus must be relatively small to avoid the creation of excessive internal stresses within the lattice. Therefore, by determining the number of atoms of B which can agglomerate into a single cluster before the geometric disregistry becomes so great that the positions of the A atoms can no longer influence the positions taken by the B atoms, a limit may be placed on the size of effective nuclei. The entire argument which follows is based upon experimentally determined orientation relations and neglects strains resulting from the complete or partial accommodation of one lattice to the dimensions of another,[5, 6] as data on this are still very meager.

As a first approximation, geometrical considerations lead to the selection of 50 percent as an arbitrary but reasonable upper limit to place upon the amount of disregistry which can occur between the atomic positions of the nucleus and those of the parent phase. This is illustrated by Fig. 1, in which the atoms of the matrix A on a plane with a cubic array are represented by dots; the atoms of the new

[1] G. Tammann, *Lehrbuch der Metallkunde* (Leopold Voss, Leipzig, Germany, 1932).
[2] R. F. Mehl and co-workers, "Studies upon the Widmanstätten Structure," A. I. M. M. E. Trans. **1–9** (1931 and following).
[3] G. Sachs, *Praktische Metallkunde*, 3rd Part (Julius Springer, Berlin, 1935), p. 25.
[4] C. A. Sloat and A. W. C. Menzies, J. Phys. Chem. **35**, 2005–2021 (1931).
[5] G. I. Finch and A. G. Quarrell, Proc. Roy. Soc. **A141**, 398 (1933).
[6] R. F. Mehl, E. L. McCandless, R. N. Rhines, Nature **134**, 1009 (1934).

phase B, also with a cubic array on the composition plane but with a 10 percent greater spacing, are represented by crosses and numbered. If 1 is the first atom of the new phase, the atoms 2, can form about it with only 10 percent disregistry; all of the 3 atoms will have a 20 percent disregistry; etc.; the 6 atoms will all have a disregistry of 50 percent. All of the B atoms numbered below 6 fall nearer to one particular A atom than to any other and their positions and stability are probably influenced by these A atoms; however the 6 atoms are equidistant between at least two A atoms and it is reasonable to assume that their positions are determined by the B atoms already present rather than by the A lattice. Thus 50 percent may be safely selected as the maximum permissible disregistry in the nucleus.

There are reasons for supposing that the allowable disregistry is actually much lower than this. The orientation studies in alloy systems are listed in Table I; the amount of disregistry in two important directions of the composition plane is given in column 2; the maximum is 13.5 percent while the average is much lower, indicating that the fit between the two lattices must be of this order for a stable nucleus to form. Hume-

TABLE I.*

1. System	2. % Disregistry in the given direction	3. Atoms along direction in nucleus with 50% disregistry	4. Atoms along direction in nucleus with 50% disregistry
Fe, allotropic transformation f.c.c. γ →b.c.c. α	13.5 [100]α 1.6 [111]α	9 63	3 21
Cu-Zn, pptn. of α from β	4. [110]α 10.9 [110]α	25 11	9 3
Cu-Sn, pptn. of α from β	1. [110]α 12.5 [110]α	101 9	31 3
Ag-Zn, pptn. of α from β	3.6 [110]α 10.4 [110]α	29 11	9 3
Al-Cu, pptn. $CuAl_2$ from Al sol. soltn.	12.6 [210] $CuAl_2$	9	3
Au-Cu, transf. f.c.c. →f.c. tet.	2.9 [100] tet. 3.9 [001] tet.	35 27	11 9
Cu-Ag, pptn. of Cu sol. soltn. from Ag sol. soltn.	11.5 All directions	9	3
Cu-Ag, pptn. of Ag sol. soltn. from Cu sol. soltn.	13.0 All directions	9	3

* Many other systems have been studied which involve practically no change of interatomic dimensions, or for which the orientation relationships are not entirely certain.

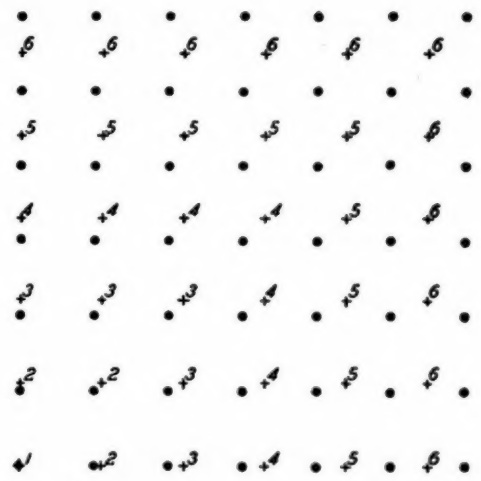

FIG. 1. Matching between atoms of a matrix A and a new phase B. The interatomic distances on the match plane of B are 10 percent greater than those on A. The dots are atoms of matrix, A. The crosses are atoms of new phase, B.

Rothery[7] finds that appreciable solid solution does not occur when the normal spacing of the two components differs by more than 14–15 percent, indicating that greater strains require the formation of a new lattice. Royer,[8] from a consideration of over 80 different examples of salt overgrowths, concludes that oriented overgrowths of different crystal species may occur when the geometrical distribution of atoms on the two cooperating planes is similar and the interatomic distances coincide within 10–15 percent. Sloat and Menzies are in substantial agreement with Royer, although they found exceptional cases where the parameters differed by as much as 30 percent. Thus, a large body of experimental evidence indicates that orienting forces are actually ineffective when the disregistry is much more than 15 percent. This is based upon interatomic distances only and if we allow that this is the total disregistry which may build up over a series of atoms it will only affect the final limit of nuclear size in the conservative direction. Column 3 of Table I gives the number of atoms in a given direction of the nucleus if 50 percent disregistry is allowed. This number is 11 for the case illustrated in Fig. 1,

[7] William Hume-Rothery, *The Structure of Metals and Alloys* (Inst. of Metals Monograph and Report Series, No. 1), (Institute of Metals, London, 1936), p. 52.

[8] M. L. Royer, Bull. Soc. Franc. Mineralogie, **51**, 9–159 (1928).

since the atoms may build up to both the left and right of the initial one, $50\times2/10+1=11$. Similarly column 4 gives the number of atoms along a chosen direction of the nucleus if a disregistry of only 15 percent is allowed.

By the reasoning already outlined, the nuclues in these solid metal reactions would not contain more than 9 atoms in a given direction if we consider a disregistry of 50 percent as the limiting value, if the more probable value of 15 percent is chosen a stable nucleus is formed when only 3 atoms align themselves in the new lattice. The low values have been selected from each column since we are seeking to limit the size of the nucleus and it is obvious that when the lattice matching is good the new nucleus may have formed before any appreciable disregistry has been built up. For example, in the Cu-Sn system one hundred and one atoms of the α phase may form before a disregistry of 50 percent has been built up, but the Cu-Ag system indicates that all of these were not required for the nucleus and that nine would have been sufficient. Apparently for a cubic array of atoms, as illustrated by Fig. 1, a group of 9 atoms, 3 in two mutually perpendicular directions would constitute a stable nucleus for the new phase.

It is recognized that these ideas do not constitute a complete interpretation of nuclear formation. Other factors, such as chemical forces, all of which may be included in the free energy of the two phases involved, undoubtedly play an important role. However, in the metal reactions with which this discussion is primarily concerned the two phases A and B are in equilibrium with each other so that $\Delta F=0$ and, experimentally, departures from this condition need be only infinitesimally small. Furthermore, the orientation relations described represent the result of the simultaneous operation of all such factors and, even though the relative importance of each factor cannot be determined, the end result must be accepted as an experimental fact.

The probable mechanism for the growth of a Na crystal from the vapor phase has been considered theoretically by Taylor, Eyring and Sherman,[9] who conclude that a three-dimensional group of eight atoms of the lattice would not be as stable as a massive crystal, but would have about the same energy as four molecules of the vapor. Thus the tendency for further growth of this cluster should be about equal to its tendency to decompose. The same condition was found for a group of four atoms at the corners of a square. The orientation studies in metals[2] as well as the overgrowth investigations[4, 8] indicate that good matching in two dimensions only is sufficient to produce definite orientation relations between the phases involved. Indeed it seems highly probable that when an atom of a new phase is surrounded by all the atoms which it would normally have as nearest neighbors in this plane of the lattice, the aggregate is sufficiently stable to act as a nucleus for crystal growth.

Therefore, from a consideration of the geometric matching and orientation relationships found in metal systems it is concluded that in such systems a stable nucleus does not contain more than about 100 atoms, while it is quite probable that about 10 atoms are actually sufficient.

[9] H. S. Taylor, H. Eyring and A. Sherman, J. Chem. Phys. 1, 68–76 (1933).

Vibrations of Asymmetrical Collinear Triatomic Molecules

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(Received April 8, 1937)

Expressions are derived for the vibration frequencies of asymmetrical collinear molecules of the X_2Y and XZY types. They are applied to the calculation of the frequencies of the N_2O^{18} molecule using an appropriate approximate potential function. The ratio of the distribution functions for N_2O^{16} and N_2O^{18} and the value of the equilibrium constant for the reaction $N_2O^{16}+H_2O^{18}\rightleftarrows N_2O^{18}+H_2O^{16}$ are also given.

WHILE vibrations of three particle systems have been studied by Cross and Van Vleck,[1] their general formulas are not suitable for the particular case of the collinear molecule. Since molecules of this type might be of some interest, however, expressions are derived here for their vibration frequencies.

According to group theory or symmetry considerations two of the vibrations of the X-Z-Y molecule are along the molecular axis, and the frequencies are the roots of a quadratic equation. The vibration perpendicular to the axis is double and the corresponding frequency is a linear function of the force constants.

Explicit formulas will be derived chiefly for the special case of the X-X-Y molecule, since the more general expressions are rather cumbersome. The degree of symmetry of the molecule is unchanged by this simplification so that the discussion concerning the special types of potential energy could also be applied to the X-Z-Y case.

Consider the X_2Y molecule. We denote by s the mutual displacement of the X atoms and by x and y the components of the displacement of the Y atom relative to the center of the X–X distance; x being in the direction of the molecular axis and y perpendicular to it. The most general quadratic potential function consistent with geometrical symmetry is written in terms of four force constants:

$$V=\tfrac{1}{2}(Ax^2+Bs^2+Cy^2+2Dxs).$$

Let m be the mass of the X atoms, M that of the Y atom, q_{XX} the (equilibrium) distance between the X atoms, q_{XY} the distance between the Y atom and the X atom nearest to it, and $q=q_{XX}+q_{XY}$. If $\alpha=q_{XX}/(2q_{XY}+q_{XX})$ and $\mu=M/(M+2m)$ the kinetic energy has the form:

$$T=\tfrac{1}{2}m[2\mu\dot{x}^2+\tfrac{1}{2}\dot{s}^2+2\alpha^2\dot{y}^2(1+\alpha^2/\mu)^{-1}].$$

If in the more general case we let n be the mass of the Z atom, m and M still referring to the X and Y atoms, respectively, the kinetic energy is expressed as:

$$T=\tfrac{1}{2}\{(m+n)\mu'\dot{x}^2+\tfrac{1}{4}[(m+n)-(m-n)^2\mu'/M]\dot{s}^2 +(m-n)\mu'\dot{x}\dot{s}+4mn\alpha^2\dot{y}^2[(m+n)(1+\alpha^2/\mu') +2\alpha(m-n)-(m-n)^2\alpha^2/M]^{-1}\};$$
$$\mu'=M/(m+n+M).$$

For X_2Y the parallel frequencies ω_1 and ω_3 are the roots of:

$$m^2\lambda^2-m\lambda(\tfrac{1}{2}A/\mu+2B)+(AB-D^2)/\mu=0,$$

and the perpendicular one ω_2 is given by:

$$m\lambda-\tfrac{1}{2}C(1/\alpha^2+1/\mu)=0.$$

In the latter case the isotopic shift can be found directly. If asterisks refer to the less abundant isotope, then:

$$\lambda_2/\lambda_2{}^*=\omega_2{}^2/\omega_2{}^{*2}=(\mu^*/\mu)(\mu+\alpha^2)/(\mu^*+\alpha^2).$$

The structural constant α can in principle be obtained from the observed values for the moment of inertia I and the length q of the molecule. The three quantities are related by:

$$I=2mq^2(\alpha^2+\mu)/(1+\alpha)^2.$$

To determine the isotopic shifts for the parallel frequencies a simplifying assumption concerning the intramolecular forces is necessary, since it is impossible to obtain the three constants A, B and D from the two experimentally observed frequencies. As a first approximation it would be natural to suppose that there is no component

[1] P. Cross and J. Van Vleck, J. Chem. Phys. **1**, 350 (1933).

of the force between the end atoms parallel to the molecular axis and write

$$V_{\text{parallel}}=\tfrac{1}{2}(k_{XX}\delta q_{XX}^2+k_{XY}\delta q_{XY}^2),$$

where the notation is self-explanatory. This assumption is equivalent to letting $D=-\frac{1}{2}A$.

However, when an attempt is made thus to determine the constants A, B and D for N_2O complex values are obtained. All calculations are based on the following set of experimental data:[2]

$$\omega_1=1288.7\ \text{cm}^{-1},$$
$$\omega_2=588.3,\quad I=66.0\times10^{-40}\ \text{gcm}^2,$$
$$\omega_3=2237.9.$$

Also electron diffraction experiments[3] give

$$q=(2.38\pm.08)\times10^{-8}\ \text{cm}.$$

Since our first approximation does not hold for N_2O, we write

$$V_{\text{parallel}}=\tfrac{1}{2}(k_{XX}\delta q^2{}_{XX}+k_{XY}\delta q_{XY}^2+2u\delta q_{XX}\delta q_{XY})$$

and assume that the interaction term u has the smallest possible value which gives rise to real values of A, B and D. This assumption has the further advantage of removing the usual ambiguity in the case when the force constant are calculated from a quadratic equation,[4] for it leads to an equation with a double root. The numerical values obtained on this assumption for the force constants of N_2O are:

$$A=14.72\times10^5\ \text{dynes/cm},\quad B=17.20,\quad D=-7.08,$$

or $\quad k_{NN}=13.80,\quad k_{NO}=14.72,\quad u=0.278.$

From these values the parallel frequencies of N_2O^{18} are calculated to be

$$\omega_1{}^*=1252.7\ \text{cm}^{-1},\quad \omega_3{}^*=2219.2.$$

The numerical evaluation of α is necessary to find the isotope shift for the perpendicular frequency. It so happens, however, that for N_2O the experimentally observed values of I and q give a complex value for α. Since the moment of inertia is known quite accurately, it is necessary that $q\leq2.31\times10^{-8}$ cm in order that α be real. If q has its largest possible value, $\alpha=4/11$. This gives $q_{NN}>q_{NO}$ by about 14 percent which may be compared with $q_{NN}=1.094\times10^{-8}$ cm and $q_{NO}=1.146$ in the diatomic case. In view of the uncertainty in the value of q it was considered best to assume $q_{NN}=q_{NO}$, i.e., $\alpha=1/3$. This corresponds to a value of q which is smaller than the maximum value by only a few units in the third decimal place. The results are not affected appreciably by any small change in α. If $\alpha=1/3$, $I^*=69.83\times10^{-40}$ gcm^2 and $\omega_2{}^*=582.4$ cm^{-1}.

These values of the isotopic shifts may be used to calculate the ratio of the distribution functions f for N_2O^{16} and N_2O^{18}, also the value of the equilibrium constant K for the reaction

$$N_2O^{16}+H_2O^{18}\rightleftarrows N_2O^{18}+H_2O^{16}.$$

This might be of some interest for the separation of oxygen isotopes. The necessary formulas have been derived by Urey and Greiff.[5] With the use of their formulas we find that at 273.1° abs.:

$$f(N_2O^{18})/f(N_2O^{16})=1.346.$$

Combining this result with the value[5]

$$f(H_2O^{18})/f(H_2O^{16})=1.274,$$

we find $K=1.056$.

In conclusion I want to thank Professor Urey who suggested these calculations.

[2] E. F. Barker, Phys. Rev. **41**, 369 (1932).
[3] R. Wierl, Ann. d. Physik **8**, 521 (1931).
[4] J. E. Rosenthal, Phys. Rev. **49**, 535 (1936).
[5] H. C. Urey and L. J. Greiff, J. Am. Chem. Soc. **57**, 321 (1935).

Theory of Surface Tension of Aqueous Solutions of Dipolar Ions

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A theory of surface tension of solutions of the dipolar ions is proposed. The theory is based on the idea of "image force" at the boundary of air and water. The experimental facts are satisfactorily accounted for by the theory.

1

IT is well known that the surface tension of solutions of inorganic salts is greater than that of the solvent.[1] To explain the phenomena various theories most of which are based on the Debye-Hückel theory of strong electrolyte have been proposed.[2-6] The solutions of inorganic acids behave differently from the solutions of inorganic salts in that the acid solutions give rise to a decrease of surface tension of the solution. This phenomenon was explained quantitatively by the assumption that the hydrogen ions of the acid solutions are adsorbed at the surface of the liquid due to the "hydrogen bond" formation with molecules of water.[7] The surface tensions of aqueous solutions of practically all organic compounds is less than that of water, though a curious exception is afforded by certain sugars.[8] Now there is a class of organic molecules, most familiarly represented by the amino acids, which exist in solution preponderantly as dipolar ions, or zwitter ions.[9] The surface tension of aqueous solutions of dipolar ions may be either greater or smaller than that of water depending largely on the magnitude of the electric moment of the dipolar ions.[10] The aqueous solutions of dipolar ions are different from the solutions of nonpolar organic compounds particularly in the fact that the increment of surface tension per mole of solute is very small, even smaller than that of the solutions of inorganic salts. No theory has yet been proposed to explain the surface tension behavior of the solutions of the dipolar ions. The present paper gives a theory which explains quantitatively the surface tension of such solutions.

[1] Heydweiller, Ann. d. Physik **33**, 145 (1910).
[2] Wagner, Physik. Zeits. **25**, 474 (1924).
[3] Onsager and Samaras, J. Chem. Phys. **2**, 529 (1934).
[4] Oka, Physico-Math. Soc. Jap. **14**, 649 (1932).
[5] Shiba, Bull. Inst. Phys. Chem. Res. Tokyo, **13**, 109 (1936).
[6] Ariyama, Bull. Chem. Soc. Jap. **11**, 687 (1936).
[7] Ariyama, Bull. Chem. Soc. Jap. **12**, 109 (1937).
[8] Traube, J. Prakt. Chem. **31**, 177 (1885); Clark and Mann. J. Biol. Chem. **52**, 157 (1922).
[9] For a discussion of dipolar ions, see Cohn, Am. Rev. Biochem. **4**, 93 (1935).
[10] J. A. Pappenheimer, Lepie and Wyman, J. Am. Chem. Soc. **58**, 1851 (1936).

2

The most important characteristic of the dipolar ions is their extremely large electric moment, which accounts for much of their behavior. Thus it is natural to suppose that the surface tension of the solutions of the dipolar ions is also greatly influenced by the electric field due to the large dipole moments of the ions.

Now let us consider the dipolar ion of electric moment μ situated in the liquid at a distance r from the surface of the water. There will be a force acting on the ion due to the image dipole of moment $j\mu$ situated at a distance r above the water surface, where $j=(D-1)/(D+1)$, D being the dielectric constant of the solution. The potential energy of the interaction of these dipoles is given by

$$u=(j\mu^2/8r^3D)(2\cos^2\theta+\sin^2\theta),$$

where θ is the angle the dipole makes with the normal to the surface of the water. The probability of the dipole lying at a distance between r and $r+dr$, and at an angle θ and $\theta+d\theta$ will be proportional to

$$2\pi e^{-u/kT}\sin\theta\, dr d\theta,$$

where θ can vary from 0 to π.

If n_0 is the total number of dipolar ions per cm^3, then the number of dipolar ions having an orientation between θ and $\theta+d\theta$, and lying at a distance from the surface between r and

$r+dr$ is

$$2\pi n_0 e^{-u/kT} \sin\theta \, dr d\theta.$$

Thus the number of ions adsorbed at the surface will be given by

$$\Gamma = 2\pi n_0 \int_a^\infty \int_\pi^0 [e^{-(j\mu^2/8r^3DkT)(1+\cos^2\theta)} - 1] d\cos\theta dr,$$

where a is the distance of nearest approach of a dipolar ion to the surface. If $u \ll kT$ then the above integral can be approximated by

$$\Gamma = -2\pi n_0 \int_a^\infty \int_\pi^0 \left[\frac{j\mu^2}{8r^3DkT}(1+\cos^2\theta)\right] d\cos\theta dr$$

$$= \frac{-2\pi n_0 j\mu^2}{6a^2DkT}.$$

The assumption that $u < kT$ is justified may be seen as follows: Assuming the magnitude of the electric moment $\mu = 20\times10^{-18}$ e.s.u. at 300°K, $D=80$, $j=1$, the value of u/kT becomes 2, 1, 0.6 and 0.37, respectively, as the value of $2r$ takes on values 4, 5, 6, 7A. Since for glycine μ is evaluated[11] to be $\mu = 15\times10^{-18}$ e.s.u. and the radius of the dipolar ion $a = 2.8$A, the condition of $u < kT$ is satisfied even for the distance of nearest approach.

According to the theorem of Gibbs the adsorption Γ_0 which is expressed in moles per cm² is related to the surface tension by the following equation.

$$\Gamma_0 = -\frac{C}{RT}\left(\frac{\partial\sigma}{\partial C}\right),$$

where σ is the surface tension of the solution, C the molar concentration of the solute per liter of the solvent. Comparing the expressions for Γ and Γ_0 we obtain

$$\frac{\partial\sigma}{\partial C} = \frac{2\pi j\mu^2 N}{6a^2D}\times10^{-3},$$

where N is Avogadro's number. The factor 10^{-3} is due to the change from the number of dipolar ions per cm³ to the number per liter.

Now, for glycine we have $\mu = 15\times10^{-18}$ e.s.u. $a = 2.8$A. Assuming $D=80$, we obtain for the right-hand side of the above equation the value 2.24. The experimental value[12] for $\Delta\sigma/\Delta C$ is 0.92, which is of the right order of magnitude. The difference of 1.32 between the theory and the experiment may be explained in the following manner. In the above discussion we have entirely neglected the effects other than the repulsive force due to the mirror image of the dipolar ions. As we have stated before almost all organic compounds are positively adsorbed at the surface of water. Thus it is reasonable to suppose that there are attractive forces acting on the dipolar ions in addition to the repulsive force which we have considered previously. The magnitude of the attractive force which the organic molecules experience at the surface of water can be estimated in the following way. We have known from the experimental researches that the logarithms of the activity coefficients of amino acids and peptides are as a first approximation proportional to their dipole moments.[13] It is also known from experiments and from the theory which we have just given that the effect of increasing the dipole moment without otherwise altering a molecule is to increase the molar increment of the surface tension of the solution. This may be seen from Table I for α and β alanine, α and β aminobutyric acid, or better still, α and ϵ aminocaproic acid. Thus we can extrapolate the curve which relates the molar increment of the surface tension and the logarithm of the activity coefficient to unit activity coefficient, this point corresponding to the zero value of the dipole moment of the dipolar ion. The molar increment of the surface tension formed by this method is always negative indicating a decrease of the surface tension of the solution if a dipole moment is absent provided that the molecule has not been changed otherwise. Using the solubility data listed in Table I, we get $\Delta\sigma/\Delta C = -0.35$ for alanine and $\Delta\sigma/\Delta C = -43$ for aminocaproic acid. Since we have no surface tension data for diglycine or triglycine we cannot estimate the molar increment of surface tension for these molecules without dipole. However, it may be expected that the molar increment of

[11] Kirkwood, J. Chem. Phys. **2**, 351 (1934).

[12] J. A. Pappenheimer, Lepie and Wyman, J. Am. Chem. Soc. **58**, 1851, (1936).

[13] E. J. Cohn, Chem. Rev. **19**, 241 (1936).

TABLE I.*

NAME	INCREMENT OF SURFACE TENSION PER MOLE/LITER OF SOLUTE $\Delta\sigma/\Delta C$ σ in dynes/cm	LOG OF SOLUBILITY RATIO IN WATER-ETHANOL SYSTEM LOG N/N_0
α Alanine	+0.58	
β Alanine	+0.77	−2.856
Glycine	+0.92	−3.139
α Aminocaproic acid	−23	−1.414
ϵ Aminocaproic acid	−0.25	−2.972
α Aminobutyric acid	−0.41	
β Aminobutyric acid	+0.05	

* Taken from Pappenheimer, Lepie and Wyman, J. Am. Chem. Soc. **58**, 1851 (1936); Cohn, McMeekin, Edsall, and Weare, J. Am. Chem. Soc. **56**, 2270 (1934); **57**, 626 (1935); **58**, 2173 (1936).

surface tension without dipole for glycine will be about the same or little larger than that of alanine. Thus the difference of 1.32 for glycine between the theoretical and experimental values may be due to the positive adsorption tendency of the molecules without the dipole, and this value may be considered quite reasonable. Thus we may consider that the theory of surface tension of the dipolar ions based on the image force idea explains the experimental facts quite satisfactorily.

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Thermodynamic Functions for Molecules Having Restricted Internal Rotations

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The partition function is considered for molecules having restricted internal rotations, and expressions are obtained which are reasonably accurate for most actual molecules. Tables are presented which list the contributions of a single restricted rotational degree of freedom to the entropy, energy, free energy, and heat capacity.

THE presence of a potential barrier of about 3000 cal./mole restricting rotation about the single bond in ethane, which was shown to exist by Kemp and Pitzer[2] and confirmed by Howard,[3] suggests that the internal rotations of a large number of molecules may be appreciably hindered. It is therefore desirable that as general and simple a procedure as possible be developed for calculating the thermodynamic functions of these molecules. Assuming a reasonable shape of restricting potential, the pertinent theory will be briefly discussed and tables presented, which make possible easy and quite accurate calculations of the complete rotational contribution to the entropy, energy, and heat capacity of almost any molecule. The moments of inertia and potential barriers must, of course, be known, unless the calculation is to be reversed, and one or more of these quantities derived from thermodynamic data. In a second paper the method here developed will be applied to a number of molecules.

Little is known concerning the exact shape of the restricting potentials, except that they must be the same qualitatively as that expressed by $\frac{1}{2}v(1-\cos n\phi)$ where v is the height and n the number of potential maxima. This, moreover, is the only form for which the mathematics has been even partially developed, and must, consequently, be adopted. For low barriers the exact shape should make little difference, while for higher barriers the shape near the minimum is the important element so that, although a somewhat incorrect height may need to be used, the thermodynamic functions should be quite accurate.

It is, of course, necessary to use approximate methods if results of general applicability are desired. In the case of high potential barriers, when the restricted rotation becomes essentially a torsional oscillation, the method commonly used with vibrating molecules is applicable. The entropy (or other thermodynamic quantity) is

[1] Shell Research Fellow, Academic Year 1936–37.
[2] Kemp and Pitzer, J. Chem. Phys. **4**, 749 (1936); J. Am. Chem. Soc. **59**, 276 (1937).
[3] Howard, Phys. Rev. **51**, 53 (1937).

TABLE I. (S_f-S) *cal./deg. mole.*

	$10^{-36}n^2/IV$								
V/RT	0	1	2	4	8	16	32	64	128
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.5	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
1.0	0.12	0.12	0.12	0.12	0.12	0.11	0.11	0.10	0.09
2.0	0.42	0.41	0.41	0.41	0.40	0.38	0.36	0.29	0.21
3.0	0.79	0.77	0.76	0.75	0.74	0.68	0.62	0.47	
4.0	1.13	1.11	1.10	1.08	1.05	0.97	0.84	0.61	
5.0	1.42	1.39	1.37	1.35	1.29	1.18	0.98		
6.0	1.66	1.62	1.60	1.57	1.49	1.34	1.08		
7.0	1.87	1.82	1.79	1.74	1.63	1.44	1.12		
8.0	2.04	1.98	1.95	1.88	1.74	1.50	1.12		
9.0	2.19	2.11	2.07	1.98	1.81	1.54			
10.0	2.32	2.21	2.16	2.06	1.86	1.55			
12.0	2.53	2.37	2.32	2.17	1.91	1.53			
14.0	2.69	2.51	2.42	2.23	1.91	1.46			
16.0	2.83	2.63	2.50	2.27	1.89	1.36			

TABLE II. $(F-F_f)/T$.

	$10^{-36}n^2/IV$								
V/RT	0	1	2	4	8	16	32	64	128
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.5	0.47	0.40	0.38	0.36	0.32	0.29	0.23	0.16	0.08
1.0	0.87	0.77	0.73	0.68	0.61	0.53	0.42	0.28	0.12
2.0	1.52	1.35	1.28	1.18	1.04	0.86	0.63	0.35	0.11
3.0	1.98	1.73	1.63	1.49	1.29	1.03	0.70	0.32	
4.0	2.33	1.99	1.85	1.67	1.43	1.10	0.70	0.26	
5.0	2.60	2.18	2.00	1.78	1.50	1.11	0.65		
6.0	2.81	2.30	2.10	1.85	1.52	1.08	0.58		
7.0	2.98	2.39	2.16	1.88	1.51	1.03	0.49		
8.0	3.13	2.45	2.20	1.89	1.48	0.96	0.38		
9.0	3.26	2.50	2.22	1.89	1.45	0.88			
10.0	3.38	2.53	2.24	1.88	1.40	0.82			
12.0	3.57	2.57	2.23	1.83	1.31	0.69			
14.0	3.72	2.59	2.21	1.76	1.20	0.57			
16.0	3.86	2.59	2.18	1.68	1.08	0.43			

taken as the sum of the translational and rotational entropies of the rigid molecule, and the entropies due to vibration, torsional or otherwise. With very high potentials one may use the harmonic oscillator or Einstein functions in which:

$$h\nu/kT=\theta/T=(nh/2\pi kT)(v/2I)^{\frac{1}{2}}$$
$$=4.463(n/T)(V/10^{40}I)^{\frac{1}{2}},$$

where I is the reduced moment of inertia (I_1I_2/I_1+I_2), n the number of potential maxima, v the height of the potential maxima in ergs/molecule, and V, the same in cal./mole. For moderately high potentials it is preferable to use the values obtained with the above potential function itself.

The quantum mechanics of the one dimensional restricted rotator has been discussed by Nielsen.[4] The wave equation in this case is easily transformed into Mathieu's differential equation:

$$M''+[\alpha+16q\cos 2x]M=0, \qquad (1)$$

where $q=\pi^2Iv/n^2h^2$ and $E-v/2=n^2h^2\alpha/32\pi^2I$.

The single value condition requires, in general, solutions for which the characteristic values α are not known; however, it can be shown that the characteristic values for these solutions must lie in regions which are closely enough bounded so as to allow a reasonably accurate partition function to be calculated. It is convenient to take the ratio of this function to the partition function of the free rotator, since this ratio depends on only two variables (V/RT) and (n^2/IV). By means of numerical sums the above partition function ratio and its first two temperature derivatives were calculated for a range of values of each of the two variables. (These calculations were actually made for the case $n=2$ and $I_1=\infty$, $I_2=I$, which involves only the ordinary Mathieu functions, for which some characteristic values have been tabulated by Ince[5] and Goldstein[6] and others were calculated as needed. The results, however, are quite accurately applicable to the general case, as stated above.) The results thus obtained for the quantities (S_f-S), $(F-F_f)/T$, H/T and C are listed in Tables I, II, III and IV. The absolute values of S and F/T are given by the equations:

$$S=R(-0.767+\tfrac{1}{2}\ln T+\tfrac{1}{2}\ln I\times10^{40}-\ln n)$$
$$-(S_f-S), \qquad (2)$$

$$-F/T=R(-1.267+\tfrac{1}{2}\ln T+\tfrac{1}{2}\ln I\times10^{40}$$
$$-\ln n)-(F-F_f)/T, \qquad (3)$$

where n is the symmetry number of the free rotator which will ordinarily be the same as the n in the potential function. If there are n potential minima, at least approximately equal, yet the molecule is not identical in the various equilibrium positions, an approximate treatment may be obtained with the n's not the same. A

[4] Nielsen, Phys. Rev. **40**, 445 (1932). See also Pauling, Phys. Rev. **36**, 430 (1930); Teller and Wiegert, *Nachr. Ges. Wiss. Göttingen. Math. physik. Klasse.* (1933) p. 218.

[5] Ince, Proc. Roy. Soc. Edinburgh, **46**, 316 (1925–26).

[6] Goldstein, Trans. Camb. Phil. Soc. **23**, 303 (1927).

case of this sort, *n*-butane, will be discussed in the following paper.

As the potential barrier becomes lower the uncertainty in the above treatment becomes greater, since the molecule spends an increasing fraction of the time in configurations appreciably different from the equilibrium one. In order to investigate this situation a study will be made of the limiting high temperature (or large moment of inertia) form of the partition function:

$$Q=\frac{1}{h^m}\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}\int_{\alpha_m}^{\beta_m}\cdots\int_{\alpha_1}^{\beta_1} e^{-1/kT(K.E.+\Phi)} \times dq_1\cdots dq_m dp_1\cdots dp_m, \quad (4)$$

where $K.E.$ and Φ are the kinetic and potential energies, respectively, m the number of rotational degrees of freedom, and α_1, β_1 the range of the ith angular coordinate. Edinoff and Aston[7] have shown that this form gives a very satisfactory approximation in the case of free rotation, while for small barriers the degree of approximation may be estimated by noting the variation of the functions in Tables I to IV with (n^2/IV), holding (V/RT) constant. The first column $(n^2/IV=0)$ was calculated with the aid of this limiting function as is explained below. Using the results of Edinoff and Aston[7] who discussed the integration with respect to the momenta, one obtains:

$$Qr=\frac{(2\pi kT)^{m/2}}{h^m}\int_{\alpha_m}^{\beta_m}\cdots\int_{\alpha_1}^{\beta_1}[A]^{\frac{1}{2}} \times e^{-\Phi/kT}dq_1\cdots dq_m, \quad (5)$$

where $[A]$ is the determinant of

$$2K.E.=\sum_{i,\,j=1}^{m} A_{ij}\dot{q}_i\dot{q}_j$$

and Φ may be expressed:

$$\Phi=\sum_{i=4}^{m}\tfrac{1}{2}v_i(1-\cos n_i q_i).$$

It may be noted at this point that the limits of integration of all internal coordinates will be 0 and 2π and that by substituting $q_1'=n_1q_1$ the n's may be removed except possibly for the factor $[A]^{\frac{1}{2}}$. For many molecules one may take

$$[A]=\sin^2 q_1\prod_{i=1}^{m} I_i$$

in which the I's are all constants, moments of inertia. This gives:

$$Qr=\frac{(2^9\pi^7k^3T^3I_1I_2I_3)^{\frac{1}{2}}}{h^3}\prod_{i=4}^{m}\left(\frac{(2\pi kTI_i)^{\frac{1}{2}}}{h} \times\int_0^{2\pi} e^{-(vi/kT)(1-\cos x)}dx\right). \quad (6)$$

TABLE III. H/T.

	$10^{-36}n^2/IV$								
V/RT	0	1	2	4	8	16	32	64	128
0.0	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
0.5	1.43	1.36	1.34	1.32	1.28	1.25	1.19	1.12	1.04
1.0	1.74	1.64	1.60	1.55	1.48	1.41	1.30	1.17	1.02
2.0	2.09	1.93	1.86	1.76	1.63	1.47	1.26	1.05	0.89
3.0	2.18	1.95	1.86	1.73	1.54	1.34	1.07	0.84	
4.0	2.19	1.87	1.74	1.58	1.37	1.12	0.85	0.64	
5.0	2.17	1.78	1.62	1.42	1.20	0.92	0.66		
6.0	2.14	1.67	1.49	1.27	1.02	0.73	0.49		
7.0	2.10	1.56	1.36	1.13	0.87	0.58	0.36		
8.0	2.08	1.46	1.24	1.00	0.73	0.45	0.25		
9.0	2.06	1.38	1.14	0.90	0.63	0.33			
10.0	2.05	1.31	1.07	0.81	0.53	0.26			
12.0	2.03	1.19	0.90	0.65	0.39	0.15			
14.0	2.02	1.07	0.78	0.52	0.28	0.10			
16.0	2.02	0.95	0.67	0.40	0.18	0.06			

TABLE IV. C.

	$10^{-36}n^2/IV$								
V/RT	0	1	2	4	8	16	32	64	128
0.0	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
0.5	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.05	1.04
1.0	1.22	1.22	1.21	1.21	1.21	1.20	1.19	1.17	1.14
2.0	1.69	1.68	1.68	1.67	1.65	1.61	1.54	1.43	1.22
3.0	2.10	2.08	2.07	2.05	2.01	1.91	1.73	1.47	
4.0	2.29	2.27	2.25	2.21	2.13	1.98	1.73	1.34	
5.0	2.33	2.30	2.27	2.23	2.12	1.89	1.56		
6.0	2.32	2.26	2.22	2.16	2.01	1.70	1.31		
7.0	2.27	2.19	2.12	2.05	1.85	1.52	1.09		
8.0	2.22	2.11	2.04	1.92	1.68	1.34	0.91		
9.0	2.18	2.05	1.94	1.80	1.53	1.19			
10.0	2.15	1.99	1.86	1.68	1.39	1.03			
12.0	2.11	1.89	1.73	1.45	1.15	0.77			
14.0	2.08	1.81	1.61	1.24	0.93	0.55			
16.0	2.06	1.75	1.51	1.06	0.72	0.34			

[7] Edinoff and Aston, J. Chem. Phys. 3, 379 (1935).

In (6) the first factor pertains to the free rotation of the molecule as a whole while each of the other factors pertain to an internal rotation with restricting potential v_i. The integral in the latter factors has been evaluated by suitable expansions for various values of (v/kT), the results being used to obtain the contribution of a single degree of freedom to the functions (S_f-S), $(F-F_f)/T$, H/T and C as listed in the first columns of Tables I, II, III and IV, respectively. It is apparent from Eq. (6) that for this group of molecules, the treatment of the entropy as a sum of independent contributions is valid for all magnitudes of restricting potential.

Where this treatment is not exact, it is, nevertheless, a good approximation, particularly for high potential barriers. This can be seen from Eq. (5) in which the principal contribution to the integral will be from configurations for which Φ is small. Therefore, if $[A]$ varies only slowly with the coordinates, it can be removed from the integral and given the value corresponding to the configuration of minimum potential. The partition function will be most in error under this procedure in the case of free rotation, when, however, an exact value for the integral in Eq. (5) can often be obtained.[7, 8] Thus an upper limit can be set to this error for all values of the potential. For the temperature derivatives of the partition function no such simple relationship holds; however, an analysis of their behavior with a continuous and slowly varying $[A]$ indicates that the limiting error in $-F/T$ will apply in order of magnitude at least to the other thermodynamic functions. Fortunately in most actual molecules the limiting error in $-F/T$ will probably be small, of the order of 0.1 cal./deg. mole. If the uncertainty of this method is too great the proper procedure appears to be the further analysis of Eq. (5) for the individual molecule or type of molecules at hand.

The accuracy of the data in Tables I to IV is about 0.02 cal./deg. mole except for certain portions of Table IV which may contain values erroneous by 0.05 cal./deg. mole. However, considering the arbitrary form of the potential function and the approximate methods involved in application to actual molecules, the results obtained with the aid of these tables cannot ordinarily be considered significant beyond 0.1 cal./deg. mole. It should also be emphasized that this treatment will fail at very low temperatures.

As a summary, the methods of calculating thermodynamic quantities for molecules having restricted internal rotations will be briefly reviewed.

1. If (V/RT) is of the order of one or greater, the desired function is calculated for the rigid molecule and to this is added contributions from the various oscillational degrees of freedom. Unless (V/RT) is very large the contributions from torsional oscillations should be calculated from Eqs. (2) and (3) and Tables I to IV.

2. If (V/RT) is fairly large (greater than about three) this result may be considered accurate; however, if (V/RT) is smaller the result may be somewhat in error. An upper limit to the error in $-F/T$ may be found by comparing the result obtained by this method for a hypothetical molecule having free rotation, with the accurate value for that molecule.[7, 8] The limiting error thus obtained for $-F/T$ applies approximately for S, H/T and C.

3. For very small values of (V/RT) it is preferable to obtain S or $-F/T$ by applying a small correction taken from Table I or II to the value calculated for the freely rotating molecule.

[8] Kassel, J. Chem. Phys. **4**, 276 (1936); **4**, 435 (1936).

Thermodynamics of Gaseous Hydrocarbons: Ethane, Ethylene, Propane, Propylene, *n*-Butane, Isobutane, 1-Butene, *Cis* and *Trans* 2-Butenes, Isobutene, and Neopentane (Tetramethylmethane)

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It is pointed out that the assumption of completely free internal rotation in the simpler hydrocarbon molecules is probably responsible for the discrepancies between the results of previous statistical mechanical calculations and the experimental data. Using the formulas and tables of the preceding paper, calculations are presented which show that, for reasonable values of rotation restricting potentials, complete agreement can be obtained with all experimental results. The uncertainty as to the exact height and shape of these potential barriers, together with the possible errors in estimated vibration frequencies make highly precise calculations of thermodynamic functions out of the question at present. Nevertheless the general agreement with experiment indicates that the potentials and frequencies selected must be approximately correct. These molecular structure data together with the available values of heats of combustion and hydrogenation are then employed in calculations which yield thermodynamic constants and the free energy of formation as a function of the temperature in the range from 300 to 1500°K. The various calculations have been made for all of the hydrocarbons listed in the title.

THE rotational partition functions for several of the simpler hydrocarbons have been calculated with the assumption of completely free rotation about single carbon−carbon bonds.[2,3] The results of these calculations are not, however, in accord with experimental data, and in the case of ethane the error has been shown to be the assumption of free internal rotation.[4,5] These results strongly suggest that a situation similar to that in ethane exists in many other molecules. In the preceding paper[6] the procedure is given for treating molecules having restricted internal rotations; however, moments of inertia, potential barriers, and vibration frequencies need to be known. The moments of inertia for the simpler hydrocarbons can be calculated with sufficient accuracy by using the reasonably well established values of the interatomic distances, while the vibration frequencies are known or can be satisfactorily estimated in many cases. The potential barriers are not known independently for any case, but if they are obtained from thermodynamic data for a few molecules, values can sometimes be interpolated for others. It is thus apparent that purely theoretical-spectroscopic calculations of thermodynamic functions are not possible at present; nevertheless in many cases the procedure and formulas for such calculations are useful as a framework for the correlation of all experimental data available, whether thermodynamic or spectroscopic in nature. If all of the various molecular constants can be determined by this procedure, then accurate calculations of thermodynamic functions can be made just as if the spectroscopic data were complete. In the present paper the various paraffins and olefins having less than four carbon atom and tetramethylmethane are discussed from this point of view. It is found that for reasonable values of potential barriers and vibration frequencies complete agreement with all experimental data can be obtained. While it is not possible at present to make precise calculations of the free energy or other functions, reasonably accurate values of thermodynamic constants are given and approximate values are tabulated for the free energy in the region from 300 to 1500°K.

Molecular Structure Data and Calculated Entropies

In the following calculations the C−C distance was taken as 1.53A, the C=C distance as 1.36A and the C−H distance as 1.11A. The angle between single bonds from a given carbon atom was assumed to be the normal tetrahedral angle. These data suffice for the calculation of

[1] Shell Research Fellow, academic year 1936–1937.
[2] Edinoff and Aston, J. Chem. Phys. **3**, 379 (1935).
[3] Kassel, J. Chem. Phys. **4**, 276 (1936); **4**, 435 (1936).
[4] Kemp and Pitzer, J. Chem. Phys. **4**, 749 (1936); J. Am. Chem. Soc. **59**, 276 (1937).
[5] Howard, Phys. Rev. **51**, 53 (1937).
[6] Pitzer, J. Chem. Phys. **5**, 469 (1937).

TABLE I. *Translation-rotation entropies for rigid molecules.*

SUBSTANCE	S_{t+r}	S_{t+r} at 298.1°K
Ethane	$7.21+4R \ln T$	52.50
Propane	$13.33+4R \ln T$	58.62
Isobutane	$15.22+4R \ln T$	60.51
Neopentane	$14.24+4R \ln T$	59.53
(St)*n*-butane	$16.33+4R \ln T$	61.62
(Be)*n*-butane	$17.40+4R \ln T$	62.69
Isobutene	$15.76+4R \ln T$	61.05

moments of inertia and thereby translation-rotation partition functions for either a rigid molecule or a freely rotating one. The resulting entropies for the latter case have been presented by Kassel[3] while those for the former appear in Table I.

The vibration frequencies of the simpler hydrocarbons have been discussed by Kassel[3, 7] and the treatment used here will be very similar, including, however, more recent experimental results. The vibrations of the hydrogens are grouped into three classes: those involving primarily C−H bond distances, H−C−H bond angles, and H−C−C bond angles. The frequencies of vibrations of the first type are always very near 3000 cm^{-1} and may be taken as such without appreciable error. Each hydrogen contributes one such frequency. The H−C−H bending frequencies are 1306 (triple) and 1536 (double) in methane;[8] 1460, 1370, 1480 (double), and 1460 (double) in ethane;[5] 1342 and 1443 in ethylene.[9] For these vibrations an averaged frequency of 1440 cm^{-1} will be used. Each methyl group contributes three such frequencies, while each methylene group contributes one. The third type of vibrations, which depend essentially on the H−C−C angle, have the lowest frequencies and are therefore the most important. Ethane has two such frequencies, each double. The value 827 cm^{-1} can be definitely assigned to one of these. The other has been estimated as 1005 cm^{-1} by Howard[5] from a force constant calculation, and as 1160 cm^{-1} by Kemp and Pitzer[4] from a consideration of gas specific heat data. In ethylene[9] the frequencies of this group have the values 1100, 950, 950, and 940 cm^{-1}. Although the frequencies for ethylene appear to be slightly higher than those for ethane, the difference is insignificant for the present purpose and the value 950 cm^{-1} will be used throughout. Each methyl group has two such frequencies, each $-CH_2-$ group three, each $=CH_2$ group two, and each CH group two. The total number of degrees of freedom in each class is shown in Table II for a number of molecules.

The vibrations of the carbon skeleton are easily classified as bending or stretching modes. From both the available spectral data and the calculations of Kassel,[7] it is apparent that for each C−C bond there is a frequency near 1000 cm^{-1}. The data on ethylene[9] suggest that

[7] Kassel, J. Chem. Phys. **3**, 326 (1935).
[8] Childs, Proc. Roy. Soc. **A153**, 555 (1936).
[9] Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

TABLE II. *Data concerning internal degrees of freedom.*

SUBSTANCE	CARBON SKELETON VIBRATIONS	HYDROGEN VIBRATIONS 950	1440	3000	TORS. VIB.	S AT 298.1°K	RESTRICTED ROT. V, $I\times10^{40}$	S_{TT} AT 298°K
Ethane	1000 (1)	4	6	6		0.62	3000, 2.7 (1)	1.70
Propane	380 (1), 1000 (2)	7	7	8		2.12	3400, 4.7 (2)	4.0
Isobutane	380 (3), 1000 (3)	8	9	10		4.44	3800, 5.2 (3)	5.9
Neopentane	380 (5), 1000 (4)	8	12	12		6.65	4200, 5.3 (4)	7.5
n-Butane	320 (2), 1000 (3)	10	8	10		4.14	3400, 5.0 (2) 3800, 18.6 (1)	7.3
Propylene	380 (1), 1000 (1), 1600 (1)	6	4	6	570 (1)	2.38	<800, — (1)	—
1-Butene	320 (2), 1000 (2), 1600 (1)	9	5	8	570 (1)	4.4	3400, 5.0 (1) <800, — (1)	—
Cis 2-butene	320 (2), 1000 (2), 1600 (1)	8	6	8	270 (1)	5.4	<800, — (2)	—
Trans 2-butene	320 (2), 1000 (2), 1600 (1)	8	6	8	270 (1)	5.4	<800, — (2)	—
Isobutene	380 (3), 1000 (2), 1600 (1)	6	7	8	570 (1)	4.6	1800, 5.2 (2)	5.7

The numbers in parentheses or in the columns under "Hydrogen Vibrations" indicate the number of degrees of freedom. The contributions to thermodynamic quantities may be calculated using tables of Einstein functions for the vibrational degrees of freedom, and using the equations and tables of the preceding paper[6] for the restricted rotational degrees of freedom. The symmetry number for the restricted rotations is three, except for the central bond of *n*-butane and 1-butene. These two rotations are discussed in the text.

for the C=C bond the value should be about 1600 cm^{-1}. The bending frequencies are much lower and consequently much more important. The values from Raman spectra[10] are for propane 374; for *n*-butane 222, 320 and 428; for isobutane 370, 438; and for tetramethylmethane 330, 416 cm^{-1}. The data for the series propane, isobutane, neopentane are thus reasonably well known and the experimental frequencies may be used; or an averaged value, 380 cm^{-1}, may be taken for each of the one, three, and five degrees of freedom, respectively, which are present in these molecules. The case of *n*-butane is less certain, since two isomers are probably present in equilibrium. This situation will be discussed below. In any event no gross error would be made if the two expected frequencies are assigned the value 320 cm^{-1}. Unfortunately data are not available for propylene or the various butenes; consequently it was necessary to make some assumption. Comparison of the bending frequencies of ethane and ethylene, as mentioned above, indicates that the carbon skeleton bending trequencies of the olefins are probably but slightly higher than those of the corresponding paraffins, and consequently the same values will be used. The selected vibration frequencies are summarized in Table II.

The only remaining data needed are those concerning the internal rotational oscillational degrees of freedom. Unfortunately these frequencies are active as fundamentals in neither the Raman nor the infrared spectra. Thus their determination by these methods is difficult at best. In the case of the double carbon – carbon bond the rotation restricting barriers are so high that the harmonic oscillator treatment is satisfactory. Bonner, in discussing ethylene, gives 825 cm^{-1} as the most probable, though not completely certain value of this frequency. Since better data are not available this value will be used to determine the force constant for all the olefins. The frequency then becomes about 570 cm^{-1} when heavy groups are substituted at one end as in propylene, 1-butene and isobutene, and about 270 cm^{-1} for both of the 2-butenes. Fortunately this frequency appears but once, so that any moderate error would not be serious. The frequency cannot be much smaller than the value given in the case of ethylene, for the total vibrational heat capacity of the gas is only 0.08 cal./deg. at 143°K.[11]

The heights of potential barriers restricting rotation about single bonds have, as yet, been determined only from thermodynamic data, although Howard[5] has employed spectral data to set a lower limit of 2000 cal./mole for the barrier in ethane. Previous calculations[4] have shown that the various thermodynamic data yield a value of 3000 cal./mole for ethane, while an application of the formulas and tables of the preceding paper[6] to the accurate third law entropy of tetramethylmethane, which was obtained by Aston and Messerly,[12] gives 4200 cal./mole for that case. Both of these values are probably correct within about 300 cal. The interpolation of 3400 cal. for propane and 3800 cal. for isobutane should be a safe procedure. The situation of the end methyl groups in *n*-butane and 1-butene is so similar to that in propane as to allow considerable confidence in the use of the same height of barrier. The central bond in *n*-butane does not have exact threefold symmetry, although there are presumably three maxima and minima. About all that can be said is that the potential maxima are probably about 3800 cal. high and that the minimum corresponding so the straightened position is most likely lowest.

The single bonds adjacent to a double bond will have a plane group on one end and a group with threefold symmetry (at least approximately) on the other end. As the two sides of the plane group become more equal, the three potential barriers will tend to be canceled out, eventually leaving six much lower ones. Consequently one would expect in propylene, 1-butene, and the 2-butenes a much lower barrier than in ethane. Actually heat and free energy of hydrogenation data indicate quite free rotation, the potential maxima being not more than 800 cal. high. Isobutane, however, has two methyl groups at the same end of the double bond, and their mutual restriction should predominate over any from the other end of the molecule, giving a higher barrier in this case. The experimental

[10] Landolt-Bornstein, *Tabellen*.

[11] Eucken and Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).

[12] Aston and Messerly, J. Am. Chem. Soc. **58**, 2354 (1936).

TABLE III. *Comparison of calculated and observed free energies for hydrogenation reactions.*

OLEFIN	$\Delta F/T_{exp}$	$\Delta F/T_{calc}$ ($V=0$)	$\Delta F/T_{calc}$ ($V=800$ cal.)
Propylene	12.16	12.26	12.37
1-Butene	12.16	12.53	12.64
Cis 2-butene	11.90	12.06	12.28
Trans 2-butene	11.02	11.24	11.46
Isobutene	9.15	(8.54)	9.38 ($V=1800$ cal.)

TABLE IV. *Comparison of calculated and third law entropies for olefin hydrocarbons at their respective boiling points.*

SUBSTANCE	b.p.	S_{exp}	S_{calc} ($V=0$)	S_{calc} ($V=800$ cal.)
Propylene	225.3	60.4	61.8	61.5
Cis 2-butene	276.8	72.7	72.4	71.9
Trans 2-butene	274.1	70.5	71.7	71.2
Isobutene	266.0	67.8	(70.5)	68.8 ($V=1800$ cal.)

In Tables III and IV, V is the potential barrier restricting rotation about bonds adjacent to the double bond.

value is 1800 cal./mole, obtained chiefly from the heat and free energy of hydrogenation, but giving some weight to the less accurate third law entropy. The resulting data regarding potential barriers are listed in Table II, while the calculations involving heat and free energy of hydrogenation data are summarized in Table III and the comparison with third law entropies in Table IV.

Before considering in detail these comparisons with experiment, the calculations for *n*-butane and 1-butene should be further discussed. All the other molecules have internal rotations involving only symmetrical methyl groups; consequently the simple treatment given in the preceding paper[6] is at once applicable for any height of potential barrier. The torsional oscillations about the double bonds are not included as rotations in the preceding statement; however, their treatment as harmonic oscillators is satisfactory.

Rotation about the middle bond in 1-butene seems to be so slightly restricted that the free rotation calculation of Kassel[3] should be quite satisfactory. A small correction can be made for a low barrier if desired.

In *n*-butane, on the other hand, the potential is large compared to RT at ordinary temperatures. Consequently, the rotational partition function should be set up for the rigid molecule in the equilibrium positions. Of these one may be described as a configuration in which the molecule is straightened out and the other two as "bent" configurations which are mirror images of each other. The translation-rotation entropies for these molecules are listed in Table I, wherein an amount $R \ln 2$ has been added to the entropy of (Be) *n*-butane because of the two optically isomeric forms present. Strictly, the internal entropy contributions would be different for the (St) and (Be) forms, however, this difference will be neglected since it is probably small but not readily ascertained. We may then write for the reaction:

$$\text{(St) } n\text{-butane} = \text{(Be) } n\text{-butane}$$

$$R \ln K = -\Delta F^\circ/T = 1.07 - \Delta H_0^\circ/T,$$

where ΔH_0° is probably positive and not more than a few hundred calories. Assuming for the moment that ΔH_0° is known, then the mole fractions N_{St} and N_{Be} can be obtained and the entropy of the mixed gas written:

$$S = N_{St}S_{St} + N_{Be}S_{Be} - R(N_{St} \ln N_{St} + N_{Be} \ln N_{Be}).$$

Although the magnitude of ΔH_0° is not known, for temperatures near 300°K, values of ΔH_0° up to 300 cal. have a negligible effect on the entropy while a value of 600 cal. reduces the entropy by less than 0.3 cal./deg. mole from the result for ΔH_0° equal to zero. Since the temperatures of interest are near or above 300°K and it seems unlikely that ΔH_0° is more than 600 cal. one may use the result for a zero value with considerable confidence. Note should be made of one additional element concerning the calculation of the entropy contribution from the torsional oscillation about the central C–C bond. While the symmetry number for a rotator would be one, nevertheless a term $(-R \ln 3)$ is introduced because only the energy levels corresponding to oscillation about one of the three minima are desired. For calculation of the quantity $(10^{-36}n^2/IV)$ or the equivalent harmonic oscillator frequency, n should be given the value three. If the existence of the different forms of *n*-butane had been neglected, and averaged values of the moments of inertia used, then the $(-R \ln 3)$ term would be omitted as

would the entropy of mixing terms which have as a maximum value, ($+R$ ln 3). This treatment, however, would be less accurate.

Comparison with Experiment

The experimental data with which comparison can be made are entropies obtained from low temperature heat capacities and combinations of heat and free energy data for hydrogenation reactions. The entropies of all of the paraffins here considered except propane are known experimentally, however the more accurate values which are for ethane and tetramethylmethane have been used to fix the heights of potential barriers. The assumptions made in the calculations for propane and isobutane were reasonably safe and very similar; consequently a satisfactory agreement in the case of isobutane will serve as confirmation of the values for both molecules. Parks, Shomate, Kennedy, and Crawford[13] obtained 67.2±1.1 cal./deg. mole for the entropy of isobutane gas at its boiling point (260.9°K) while the calculated value is 67.7 cal./deg. mole.

Huffman, Parks, and Barmore[14] obtained 72.5 cal./deg. mole for the entropy of *n*-butane at its boiling point. Recently the extropolation below liquid-air temperatures has been reconsidered by Parks and co-workers,[13] who give a revised value of 73.7 cal./deg. mole. The calculated result 72.8 cal./deg. mole lies between those obtained from the experimental data. This is a very satisfactory confirmation of the calculated value and indicates that the rather uncertain assumptions were at least approximately correct.

The heats of hydrogenation at 355°K of ethylene, propylene, and the various butenes

[13] Parks, Shomate, Kennedy and Crawford, J. Chem. Phys. **5**, 359 (1937).
[14] Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).

Table V. *Thermodynamic constants for twelve hydrocarbons in the gaseous state.*

Substances	$S°_{298.1}$ cal./deg. mole	Constants of Formation from $H_{2(g)}$ and $C_{(\beta\text{-graphite})}$ $\Delta S°_{298.1}$ cal./deg. mole	$\Delta H°_{298.1}$ kcal./mole	$\Delta F°_{298.1}$ kcal./mole	$\Delta H_0°$ kcal./mole
Methane	44.60±0.0	−19.22	−18.07±0.12	−12.34	−16.15
Ethane	54.82±0.2	−41.59	−20.60±0.23	− 8.20	−16.86
Propane	64.8 ±0.5	−64.2	−25.39±0.32	− 6.25	−20.14
n-Butane	75.1 ±1	−86.5	−30.57±0.43	− 4.78	−23.90
Isobutane	70.8 ±0.8	−90.8	−32.20±0.43	− 5.13	−25.45
Neopentane	73.7 ±0.5	−120.5	−40.7 ±1.2	−4.8	−32.4
Ethylene	52.75±0.1	−12.43	+12.09±0.25	+15.80	+14.06
Propylene	65.1 ±0.7	−32.7	+4.48±0.38	+14.23	+8.12
1-butene	75.4 ±1	−55.0	−0.41±0.5	+15.99	+4.72
Cis 2-butene	73.6 ±1	−56.8	−2.14±0.5	+14.79	+2.92
Trans 2-butene	73.0 ±1	−57.4	−3.09±0.5	+14.02	+1.97
Isobutene	71.3 ±1	−59.5	−4.02±0.5	+13.72	+0.85

The uncertainty in $S°_{298.1}$ applies also to $\Delta S°_{298.1}$ and the uncertainty in $\Delta H°_{298.1}$ to $\Delta F°_{298.1}$ and $\Delta H_0°$.

Table VI. *Values of $\Delta F°/T$ of formation for twelve hydrocarbons in the gaseous state.* (*Units: cal./deg. mole*).

T, °K	Methane*	Ethane	Propane	*n*-Butane	Isobutane	Neopentane	Ethylene	Propylene	1-Butene	*Cis* 2-Butene	*Trans* 2-Butene	Isobutene
300	−40.9	−27.0	−20.3	−15.2	−16.4	−15.1	52.8	47.7	53.7	49.7	47.2	46.1
350	−32.2	−17.0	− 8.1	− 0.5	− 0.9	+ 4.5	47.2	45.8	54.1	51.0	48.8	48.0
400	−25.5	− 9.4	+ 1.4	+10.9	+11.2	19.8	43.0	44.5	54.6	52.1	50.4	49.8
450	−20.2	− 3.2	8.9	20.0	20.7	31.7	39.9	43.6	55.2	53.2	51.7	51.3
500	−16.0	+ 1.8	15.1	27.4	28.4	41.5	37.6	43.1	55.8	54.2	53.0	52.6
600	− 9.4	9.7	24.5	38.7	40.2	56.4	34.0	42.4	56.9	56.0	55.1	54.9
700	− 4.5	15.4	31.5	47.1	49.0	67.5	31.7	42.0	57.9	57.6	56.8	56.7
800	− 0.8	19.7	37.0	53.6	55.9	76.0	30.0	41.9	58.9	59.0	58.3	58.3
900	+ 2.1	23.1	41.2	58.8	61.2	82.6	28.7	41.9	59.7	60.1	59.6	59.6
1000	4.5	25.7	44.6	62.6	65.1	87.5	27.6	41.8	60.1	60.7	60.4	60.5
1200	8.1	29.1	48.7	67.2	69.8	93.4	25.9	41.3	60.0	61.1	61.0	61.3
1500	11.8	31.5	50.9	68.8	71.8	96.2	22.8	39.0	58.1	59.7	59.6	59.9

* The values for methane are taken from Kassel, J. Am. Chem. Soc. **55**, 135 (1933).

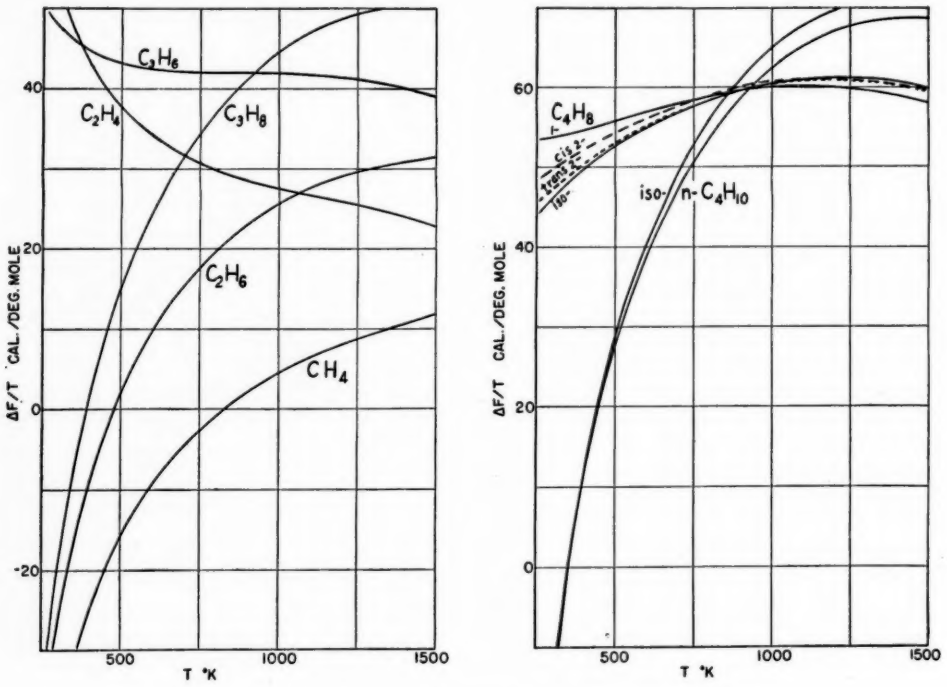

FIG. 1. The free energy of formation of gaseous hydrocarbons.

have been accurately measured by Kistiakowsky and co-workers.[15] The equilibrium constants of the same reactions have been obtained by Frey and Huppke[16] for several temperatures, including 673°K. Table III gives a comparison of the experimental values of $(-R \ln K = \Delta F/T)$ for 673°K with those calculated with the aid of the heat data. In all the olefins except isobutene, the potentials restricting rotation should be about the same, and rather small. Table III shows that the agreement is satisfactory for values up to about 800 cal., since the experimental errors may be taken as at least 0.4 cal./deg. mole. With isobutane a higher potential is expected, and a value of 1800 cal. gives a good agreement.

The experimental entropies of the olefins are all from the work of Parks and co-workers[14, 17] and have been increased over the originally published values by 10 percent of the extrapolated portion as has been recently recommended.[13] The comparison with calculated values in Table IV shows complete agreement within the experimental errors.

THERMODYNAMIC FUNCTIONS FOR TWELVE HYDROCARBONS

While the partition functions set up in the preceding paragraphs are not very precise, the general agreement of thermodynamic quantities calculated from them with experimental values indicates that they must be approximately correct. These partition functions appear to be, in fact, accurate enough for use with the best heat of formation data now available without significantly increasing the uncertainties except at high temperatures. Table V contains the values of several thermodynamic functions at 298.1°K and the values of the heat of formation at the absolute zero for twelve hydrocarbons. In Table VI the free energies of formation are listed for various temperatures in the range from 300 to 1500°K. The data of Table VI are presented graphically in Fig. 1.

In the various calculations the heats of formation of the paraffins are taken from the work of

[15] Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan, J. Am. Chem. Soc. **57**, 65 (1935); Kistiakowsky, Ruhoff, Smith, and Vaughan, ibid. **57**, 876 (1936).
[16] Frey and Huppke, Ind. Eng. Chem. **25**, 54 (1933).
[17] Todd and Parks, J. Am. Chem. Soc. **58**, 134 (1936).

Rossini,[18] while the values for the olefins are obtained by combining the heat of hydrogenation[14] with the heat of formation of the resulting paraffin. In the case of ethylene, precise heat of combustion data[19] are available and the value used is a compromise one. The remaining calculations were made using the data and methods described in this and the preceding paper.[6] All values of the constants of formation are based on H_2 gas and β-graphite. The contribution due to nuclear spin is omitted from all entropies. In obtaining the values listed in Tables V and VI the following constants were used either in the present work or that of Rossini.

For $H_{2(g)}+1/2O_{2(g)}=H_2O_{(l)}$,
$\Delta H^\circ_{298.1}=-63.313\pm0.01$ kcal./mole,

$C_{(\beta\text{-graphite})}+O_{2(g)}=CO_{2(g)}$,
$\Delta H^\circ_{298.1}=-94.24\ \pm0.10$ kcal./mole,

$C_{(\text{diamond})}=C_{(\beta\text{-graphite})}$,
$\Delta H^\circ_{298.1}=-\ 0.22\ \pm0.07$ kcal./mole,

1 kcal. = 1000 cal. = 4183.3 int. joules;

for H_2, $S^\circ_{298.1}=31.23$ cal./deg. mole

and $(H^\circ_{298.1}-H_0^\circ)=2.028$ kcal./mole;

for $C_{(\beta\text{-graphite})}S^\circ_{298.1}=1.36$ cal./deg. mole

and $(H^\circ_{298.1}-H_0^\circ)=0.25$ kcal./mole.

In Table VI some of the values have been obtained by graphical interpolation. The values for 450, 1000 and 1500°K were directly calculated while those calculated for 298.1 and 763°K (in Tables III and V) were also used in making the interpolations. The slope of the curve at 298.1°K was made to correspond to the known ΔH° at that temperature. It should be noted that the values in Table VI are not sufficiently precise to allow accurate differences to be taken. Thus heat contents and heat capacities must be calculated separately if other than very rough estimates are desired.

The data in Table VI should be useful in obtaining equilibrium constants for a large number of hydrocarbon reactions.

[18] Rossini, Nat. Bur. Stand. J. Research **13**, 21 (1934); **15**, 357 (1935); J. Chem. Phys., **3** 438 (1935).
[19] Rossini, Nat. Bur. Stand. J. Research **17**, 629 (1936).

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On the Theory of Optical Rotatory Power

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The Born theory of optical activity in quantum-mechanical form is simplified with the aid of certain approximations. It leads to a simple expression for the rotatory parameter of an active molecule in terms of the geometrical configuration and the polarizability tensors of its constituent groups. Optical anisotropy of the component groups and inhibited internal rotation are found to play an important role in determining rotatory power. The proposed theory has points of similarity both with the polarizability theories of Gray, de Mallemann, and Boys and also with Kuhn's specialization of Born's classical theory of optical activity. To illustrate its use, the absolute configuration and the specific rotation of *d*-secondary butyl alcohol are calculated.

I

A PHYSICAL theory of optical activity was first formulated by Fresnel,[1] who attributed the phenomenon to circular double refraction. In seeking a structural explanation in crystals he postulated a helicoidal arrangement of the atoms, anticipating the screw axis revealed by modern x-ray investigations of crystal structure. This type of structural explanation was inadequate to account for the optical activity of liquids and solutions, discovered by Biot.[2] It was necessary to attribute the optical rotatory power of a liquid to a characteristic structure of its component molecules, themselves, rather than to their arrangement. The principles of stereochemistry, enunciated by Le Bel and van't

[1] Fresnel, Bull. Soc. Philomat., p. 147 (1824).
[2] Biot, Bull, Soc. Philomat., p. 190 (1815).

Hoff,[3] led to the important empirical rule that the absence of a plane or center of symmetry was a necessary condition for molecular rotatory power. Drude[4] made an attempt to develop a theory of optical rotatory power both in crystals and liquids, based upon the classical theory of dispersion. However, he was forced to postulate the existence of electric charges constrained to vibrate in helicoidal paths, a point of view not substantiated by modern views of molecular structure.

A satisfactory molecular theory of optical rotatory power was first formulated by Born[5] in the frame of the classical oscillator theory of dispersion. In Born's theory, optical rotatory power is to be found in a second-order term of the dispersion formula, arising from the retardation of the radiation field over the space occupied by an active molecule. A theory similar to that of Born was almost simultaneously proposed by Oseen[6] and certain refinements were introduced by Gans.[7] The classical theory has been extensively applied by Kuhn,[8] using a special model consisting of a pair of anisotropic dispersion oscillators. Recently Born[9] has applied the theory to a model consisting of four isotropic oscillators. With the advent of quantum mechanics, Born's theory was reformulated on the basis of the quantum-mechanical theory of dispersion.[10] It is here that an adequate theory of rotatory power, free from the defects of the artificial oscillator theory, is to be sought. We shall endeavor to put the quantum-mechanical theory into manageable form with the aid of certain approximations.

Paralleling the Born theory, a theory of rotatory power, similar in principle, but starting directly from the forced vibrations produced in a molecule by the radiation field, has been developed by Gray,[11] de Mallemann,[12] and Boys.[13] We shall refer to this theory as the polarizability theory of optical activity, since it allows the expression of the rotatory power of a molecule in terms of the configuration and polarizabilities of its constituent groups. We shall show how the quantum-mechanical formulation of the Born theory leads directly to the polarizability theory when certain reasonable approximations are introduced. The initial term in the polarizability theory, which we believe to be chiefly responsible for rotatory power, has not, however, been considered by other writers on the polarizability theory, since they have either treated the groups constituting an active molecule as optically isotropic or as possessing optical axes of symmetry along the bonds linking them to an asymmetric carbon atom. The formula, which we shall obtain involves the interaction of pairs of optically anisotropic groups. Its analog in the oscillator theory is to be found in Kuhn's specialization of Born's classical formula. However, anisotropic polarizable groups replace the hypothetical dispersion oscillators, and the coupling parameter is explicitly calculated from the electrostatic interaction of the groups.

II

Optical rotatory power in a dispersive medium can be formally attributed to a difference in its refractive indices, n_r and n_l, for right and left circularly polarized light. A beam of plane polarized light may be regarded as a superposition of two right and left circularly polarized components of equal intensity. A phase difference between the two circular components is set up in an optically active medium, which is equivalent to a rotation of the plane of polarization of their resultant plane polarized wave. The angle, ϑ, through which the plane of polarization is rotated per centimeter of path is given by

$$\vartheta = (\pi/\lambda_0)(n_r - n_e), \tag{1}$$

where λ_0 is the wave-length of the light in vacuum.

[3] Le Bel, Bull. Soc. Chim. **22**, 337 (1874); van't Hoff, *La Chimie dans L'Espace* (1875).
[4] Drude, *Theory of Optics*, English translation (Longmans, 1902), p. 400.
[5] Born, Physik. Zeits. **16**, 251 (1915); *Optik* (Springer, Berlin, 1930).
[6] Oseen, Ann. d. Physik **48**, 1 (1915).
[7] Gans, Zeits. f. Physik **17**, 353 (1923); **27**, 164 (1924); Ann. d. Physik **79**, 548 (1926).
[8] W. Kuhn, Zeits. f. physik. Chemie **B4**, 14 (1929); Ber. **63**, 190 (1930); Trans. Faraday Soc. **26**, 293 (1930). Kuhn and Freudenberg, *Drehung der Polarizationsebene des Lichtes* (Leipzig, 1932).
[9] Born, Proc. Roy. Soc. London **A150**, 84 (1935); Oke, ibid. **153**, 339 (1935).
[10] Rosenfeld, Zeits. f. Physik **52**, 161 (1928); Born and Jordan, *Elementare Quantenmechanik* (Springer, Berlin, 1930), p. 250.
[11] Gray, Phys. Rev. **7**, 472 (1916).
[12] de Mallemann, Rev. Gen. Sci. **38**, 453 (1927).
[13] Boys, Proc. Roy. Soc. London **A144**, 655, 675 (1934).

From the standpoint of the electromagnetic theory,[5, 10] the optical properties of a substance may be characterized by the manner in which its electric polarization **P** and magnetic polarization **M** are related to the field vectors of an electromagnetic wave. In an isotropic optically active medium these relations have the following form

$$\mathbf{P}=\chi_e\mathbf{E}+\sigma\mathbf{H}-(\rho/c)\partial\mathbf{B}/\partial t, \qquad (2)$$
$$\mathbf{M}=\chi_m\mathbf{H}+\sigma\mathbf{E}+(\rho/c)\partial\mathbf{E}/\partial t,$$

where **E** is the electric vector, **H** the magnetic vector and **B** the magnetic induction. χ_e and χ_m are the ordinary electric and magnetic susceptibilities, and ρ is a constant which determines the rotatory power of the medium. The constant σ does not influence the rotatory power and is of no importance for our purposes. The rotation in radians per centimeter of a plane polarized wave is given by

$$\vartheta=16\pi^3\rho/\lambda_0^2. \qquad (3)$$

It is associated with a corresponding difference in the refractive indices for right and left circularly polarized light, but the decomposition of the plane polarized wave into circular components is unessential. The specific rotation, $[\alpha]$, in degrees per decimeter per gram of active substance per cubic centimeter is equal to $1800v\vartheta/\pi M$, where M is the molecular weight and v is the volume occupied by a mole of the substance.

$$[\alpha]=2.880\times10^4(\pi^2\rho v/M\lambda_0^2). \qquad (4)$$

The constant ρ can be related to a molecular rotatory parameter g. We shall presently show that the average electric moment, $\mathfrak{p}_{00'}$, induced in an active molecule by a plane electromagnetic wave can be expressed in the following form

$$\mathfrak{p}_{00'}=\alpha\mathbf{F}+\gamma(\mathbf{a}_1\times\mathbf{F})+g\nabla\times\mathbf{F}, \qquad (5)$$

where $\mathbf{a}_1$ is a unit vector normal to the wave front and **F** is the internal electric vector of the light. The Lorentz field, equal to $(n^2+2)\mathbf{E}/3$ where n is the refractive index, is a fairly good approximation to **F**, even in polar liquids for frequencies equal to or greater than those of the visible spectrum. From Maxwell's equation, $\nabla\times\mathbf{E}=-(1/c)\partial\mathbf{B}/\partial t$, and the definition of **P** as the density of electric moment, we see that the rotatory part of the electric polarization is equal to $-[(n^2+2)/3v](Ng/c)\partial\mathbf{B}/\partial t$. By comparison with Eq. (1), we obtain

$$\rho=\frac{n^2+2}{3}\frac{Ng}{v}, \qquad (6)$$

where N is Avogadro's number. The specific rotation may then be written in the form

$$[\alpha]=2.880\times10^4\frac{\pi^2N}{M\lambda_0^2}\frac{n^2+2}{3}g. \qquad (7)$$

If we insert numerical values for the constants, $[\alpha]_D$, the specific rotation for the D line of sodium, $\lambda_0=5893$A, may be calculated from the formula

$$[\alpha]_D=4.960\times10^{37}\frac{n^2+2}{3M}g. \qquad (8)$$

If the angstrom instead of the centimeter is employed as the unit of length in the calculation of the rotatory parameter, g, which has dimensions of length to the fourth power, we may write

$$[\alpha]_D=4.960\times10^5\frac{n^2+2}{3M}g, \qquad (9)$$

g, of course, depends upon the frequency of the light, but varies slowly outside regions of anomalous rotatory dispersion.

III

We shall now undertake the calculation of the molecular rotatory parameter g, following the general outlines of the theory of Born.[10] We consider a polyatomic molecule situated in a Lorentz cavity in a dispersive medium of refractive index n, through which a plane electromagnetic wave of frequency, ν, is passing. We suppose that the ground electronic state of the molecule is nondegenerate, although the ground state as a whole may have vibrational degeneracy, which is unimportant for the dispersion. The orientation of the molecule, that is to say the orientation of the average configuration of its atomic nuclei, is assumed to be fixed relative to a set of mutually orthogonal unit vectors, $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, specifying the directions of the wave normal, electric vector, and magnetic vector of the wave. Later we average over all molecular orientations. By the principle of spectroscopic stability, this is equiva-

lent to averaging over spatial quantum numbers. The Lorentz field $\mathbf{F}$ at a point, $\mathbf{R}$, referred to some convenient origin, may be written

$$\mathbf{F}=\mathbf{a}_2F\cos 2\pi[\nu t-\mathbf{R}\cdot\mathbf{a}_1/\lambda], \tag{10}$$

where the amplitude F is equal to the product of $(n^2+2)/3$ and the amplitude $\mathbf{E}$ of the electric vector. The field $\mathbf{F}$ may be derived from the following vector potential

$$\mathbf{F}=-(1/c)\partial\mathbf{A}/\partial t$$
$$\mathbf{A}=-\mathbf{a}_2(cF/2\pi\nu)\sin 2\pi[\nu t-\mathbf{R}\cdot\mathbf{a}_1/\lambda]. \tag{11}$$

From the quantum-mechanical theory of dispersion,[14] we obtain the following expression for the electric moment induced in the ground state of the molecule by the electromagnetic field.

$$\boldsymbol{\mu}_{00}'=-\frac{eF}{4\pi imh\nu}\sum_n{}'\left\{\frac{\boldsymbol{\mu}_{0n}\mathbf{p}_{n0}{}^+\cdot\mathbf{a}_2-\boldsymbol{\mu}_{n0}\mathbf{p}_{0n}{}^+\cdot\mathbf{a}_2}{\nu_{n0}+\nu}\times\exp(2\pi i[\nu t-\mathbf{R}_0\cdot\mathbf{a}_1/\lambda])\right.$$
$$\left.-\frac{\boldsymbol{\mu}_{0n}\mathbf{p}_{n0}{}^-\cdot\mathbf{a}_2-\boldsymbol{\mu}_{n0}\mathbf{p}_{0n}{}^-\cdot\mathbf{a}_2}{\nu_{n0}-\nu}\times\exp(-2\pi i[\nu t-\mathbf{R}_0\cdot\mathbf{a}_1/\lambda])\right\}, \tag{12}$$

where $\mathbf{R}_0$ specifies the position of the molecular center of gravity and the sum extends over all excited states of the molecule, associated with the spectroscopic frequencies ν_{n0}. An integral over continuous parts of the spectrum is implied in the summation. The constants h, e, and m are Planck's constant, the electronic charge, and the electronic mass. The quantities, $\boldsymbol{\mu}_{n0}$, are the matrix elements of the electric moment of the molecule, and $\mathbf{p}_{n0}{}^+$ and $\mathbf{p}_{n0}{}^-$ are matrix elements of operators defined below.

$$\boldsymbol{\mu}=\sum_s e\mathbf{r}_s=\sum_s\boldsymbol{\mu}_s,$$
$$\mathbf{p}^+=\sum_s\exp(-2\pi i\mathbf{r}_s\cdot\mathbf{a}_1/\lambda)\mathbf{p}_s$$
$$=\mathbf{p}-\frac{2\pi i}{\lambda}\sum_s\mathbf{a}_1\cdot\mathbf{r}_s\mathbf{p}_s, \tag{13}$$
$$\mathbf{p}^-=\sum_s\exp(+2\pi i\mathbf{r}_s\cdot\mathbf{a}_1/\lambda)\mathbf{p}_s$$
$$=\mathbf{p}+\frac{2\pi i}{\lambda}\sum_s\mathbf{a}_1\cdot\mathbf{r}_s\mathbf{p}_s,$$

where the sum extends over all electrons of the molecule, $\mathbf{r}_s$ is the position of electron s relative to the molecular center of gravity, $\mathbf{p}_s$ is its momentum operator, and $\mathbf{p}$ the total electronic momentum. It is sufficient to retain only the first two terms in the expansions of $\mathbf{p}^+$ and $\mathbf{p}^-$. The second terms are responsible for optical activity. Substitution of the expressions (13) in Eq. (12) yields after some algebraic simplification

$$\boldsymbol{\mu}_{00}'=[\boldsymbol{\alpha}\cdot\mathbf{a}_2+\boldsymbol{\gamma}\cdot\mathbf{a}_2]F\cos 2\pi[\nu t-\mathbf{R}_0\cdot\mathbf{a}_1/\lambda]$$
$$+(2\pi/\lambda)\mathbf{g}\cdot\mathbf{a}_2F\sin 2\pi[\nu t-\mathbf{R}_0\cdot\mathbf{a}_1/\lambda], \tag{14}$$

where the tensors $\boldsymbol{\alpha}$, $\boldsymbol{\gamma}$, and $\mathbf{g}$ are written in dyadic form below. The expression for $\boldsymbol{\alpha}$, the familiar polarizability tensor, is simplified by use of the relation, $e\mathbf{p}_{n0}=2\pi im\nu_{n0}\boldsymbol{\mu}_{n0}$,

$$\boldsymbol{\alpha}=\frac{2}{h}\sum_n{}'\frac{\nu_{n0}\boldsymbol{\mu}_{0n}\boldsymbol{\mu}_{n0}}{\nu_{r0}{}^2-\nu^2},$$

$$\boldsymbol{\gamma}=\frac{e}{\lambda mh\nu}\sum_{r,s}\sum_n{}'\frac{\nu_{n0}}{\nu_{n0}{}^2-\nu^2}[(\boldsymbol{\mu}_r)_{0n}\mathbf{a}_1\cdot(\mathbf{r}_s\mathbf{p}_s)_{n0}$$
$$-(\boldsymbol{\mu}_r)_{n0}\mathbf{a}_1\cdot(\mathbf{r}_s\mathbf{p}_s)_{0n}], \tag{15}$$

$$\mathbf{g}=\frac{e}{2\pi imh}\sum_{r,s}\sum_n{}'\times\frac{(\boldsymbol{\mu}_r)_{0n}(\mathbf{a}_1\cdot\mathbf{r}_s\mathbf{p}_s)_{n0}-(\boldsymbol{\mu}_r)_{n0}(\mathbf{a}_1\cdot\mathbf{r}_s\mathbf{p}_s)_{0n}}{\nu_{n0}{}^2-\nu^2}.$$

We need not concern ourselves further with $\boldsymbol{\gamma}$, since it does not contribute to the rotation but simply gives rise to the term $\sigma\mathbf{H}$ in Eq. (2). The tensor $\mathbf{g}$ gives rise to the rotatory power. We now average $\boldsymbol{\mu}_{00}'$ over all orientations of the molecule with respect to the fixed set of axes $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$. We make use of the formulas

$$((\mathbf{v}_1\cdot\mathbf{a}_1)(\mathbf{v}_2\cdot\mathbf{a}_1)(\mathbf{v}_3\cdot\mathbf{a}_2))_{Av}=0,$$
$$((\mathbf{v}_1\cdot\mathbf{a}_2)(\mathbf{v}_2\cdot\mathbf{a}_1)(\mathbf{v}_3\cdot\mathbf{a}_2))_{Av}=0, \tag{16}$$
$$(\mathbf{v}_1\cdot\mathbf{a}_3)(\mathbf{v}_2\cdot\mathbf{a}_1)(\mathbf{v}_3\cdot\mathbf{a}_2)=-\tfrac{1}{6}\mathbf{v}_1\cdot(\mathbf{v}_2\times\mathbf{v}_3),$$

where $\mathbf{v}_1$, $\mathbf{v}_2$, and $\mathbf{v}_3$ are any set of vectors fixed in the molecule. Thus the vector $(\mathbf{g}\cdot\mathbf{a}_2)_{Av}$ is equal to $(\mathbf{a}_3\cdot\mathbf{g}\cdot\mathbf{a}_2)_{Av}\mathbf{a}_3$ and $(\boldsymbol{\gamma}\cdot\mathbf{a}_2)_{Av}$ is equal to $(\mathbf{a}_3\cdot\boldsymbol{\gamma}\cdot\mathbf{a}_2)_{Av}\mathbf{a}_3$. From Eq. (11), we may calculate

$$\nabla\times\mathbf{F}_0=(2\pi/\lambda)F\mathbf{a}_3\sin 2\pi[\nu t-\mathbf{R}_0\cdot\mathbf{a}_1/\lambda],$$
$$\mathbf{a}_1\times\mathbf{F}_0=F\mathbf{a}_3\cos 2\pi[\nu t-\mathbf{R}_0\cdot\mathbf{a}_1/\lambda]. \tag{17}$$

[14] Sommerfeld, *Atombau und Spektralinien, Wellenmechanischer; Ergänzunsband*, p. 193, Vieweg, Braunschweig (1929); Dirac, *Quantum Mechanics*, Chap. XII, (Oxford, 1930).

Denoting $(\mathbf{a}_3\cdot\mathbf{g}\cdot\mathbf{a}_2)_{Av}$ by g and $(\mathbf{a}_3\cdot\boldsymbol{\gamma}\cdot\mathbf{a}_2)_{Av}$ by γ, we obtain from Eqs. (14) and (16)

$$(\mathfrak{y}_{00}')_{Av}=\alpha\mathbf{F}_0+\gamma(\mathbf{a}_1\times\mathbf{F}_0)+g\nabla\times\mathbf{F}_0, \quad (18)$$

which is identical with Eq. (5). The constant α is the mean polarizability of the molecule, equal to one-third of the sum of the diagonal elements of α. In carrying out the averaging of $\mathbf{a}_3\cdot\mathbf{g}\cdot\mathbf{a}_2$, we may first express the tensors $(\mathbf{r}_s\mathbf{p}_s)_{n0}$ in terms of an orthogonal set of unit vectors fixed in the molecule and then sum the result.

$$g=-\frac{e^2}{12\pi imh}\sum_r\sum_s{}'_n \times\frac{(\mathbf{r}_r)_{0n}\cdot(\mathbf{r}_s\times\mathbf{p}_s)_{n0}-(\mathbf{r}_r)_{n0}\cdot(\mathbf{r}_s\times\mathbf{p}_s)_{0n}}{\nu_{n0}^2-\nu^2}. \quad (19)$$

If we remember that the magnetic moment $\mathbf{m}$ of the molecule is given by

$$\mathbf{m}=(e/2mc)\sum_s\mathbf{r}_s\times\mathbf{p}_s \quad (20)$$

we may write g in a slightly different form

$$g=\frac{c}{6\pi ih}\sum_n{}'\frac{\mathbf{m}_{0n}\cdot\mathfrak{y}_{n0}-\mathbf{m}_{n0}\cdot\mathfrak{y}_{0n}}{\nu_{n0}^2-\nu^2}. \quad (21)$$

An analysis similar to the preceding one except for the fact that the retardation of the wave over the molecule may be neglected entirely yields for $\mathbf{m}_{00}'$, the average magnetic moment induced in the ground state of the molecule.

$$(\mathbf{m}_{00}')_{Av}=(g/c)\partial\mathbf{F}_0/\partial t+\gamma\mathbf{F}_0. \quad (22)$$

Eqs. (19) and (21) are Born's equations[10] for the optical rotatory parameter, put in a slightly more explicit form.

We shall attempt to simplify the general formula for g with the aid of certain approximations, which will allow its calculation from the properties of the groups or radicals constituting the molecule. We suppose that the molecule consists of N groups coupled to an inactive central group by valence bonds. The central group may be the asymmetric carbon atom in simple optically active organic compounds or it may be a hydrocarbon radical of rigid configuration as in the spirane compounds. The subsidiary groups may themselves be optically active as in the sugars or other compounds containing two or more asymmetric carbon atoms. When this is true, the group in question may be further decomposed into secondary groups.

The sum over all electrons in Eq. (19) may be replaced by a sum over the N+1 groups by means of the following relations

$$\sum_r(\mathfrak{y}_r)_{0n}=\sum_{i=1}^{N+1}\mathfrak{y}_{0n}{}^{(i)},$$

$$\sum_s(\mathbf{r}_s\times\mathbf{p}_s)_{n0}=\sum_{k=1}^{N+1}\left[\mathbf{R}_k\times\mathbf{p}_{n0}{}^{(k)}+\frac{2mc}{e}\mathbf{m}_{n0}{}^{(k)}\right], \quad (23)$$

$$\mathbf{m}_{n0}{}^{(k)}=\frac{e}{2mc}\sum_s{}^{(k)}(\mathbf{r}_s{}^{(k)}\times\mathbf{p}_s)_{n0},$$

where $\mathfrak{y}^{(i)}$ is the electric moment of group i, $\mathbf{p}^{(k)}$ is the total electronic momentum of group k, and $\mathbf{m}^{(k)}$ is its total magnetic moment referred to the center of gravity of group k, situated at a point $\mathbf{R}_k$ from center of gravity of the molecule as a whole. Since nondiagonal matrix elements of any constant vanish, the shift in origin from the center gravity of the molecule to the center of gravity of the group does not affect the matrix elements $\mathfrak{y}_{0n}{}^{(i)}$. The replacement of the sums over electrons by sums over groups is strictly valid only when electron exchange between groups can be neglected, since otherwise the assignment of a definite number of electrons to a given group is ambiguous. However, when structural resonance involving two or more of the groups is absent, it is an adequate approximation to neglect exchange between groups except for the bonding electrons between each subsidiary group and the central group. The ambiguity in the assignment of electrons to the various groups may then be removed by including the bonding electrons between a subsidiary group and the central group in the sums (23) for both groups with a factor, $\frac{1}{2}$, in each case. In the absence of structural resonance, electron exchange between subsidiary groups can be neglected. From Eqs. (19), (21) and (23) and the relation, $e\mathbf{p}_{n0}{}^{(k)}=2\pi im\nu_{n0}\mathfrak{y}_{n0}{}^{(k)}$, we obtain

$$g=g^{(0)}+g^{(1)}+\sum_{k=1}^{N+1}g_k,$$

$$g^{(0)}=\frac{1}{6h}\sum_{i\neq k=1}^{N+1}\sum_n{}'\frac{\nu_{n0}}{\nu_{n0}^2-\nu^2}[\mathbf{R}_k\cdot(\mathfrak{y}_{0n}{}^{(i)}\times\mathfrak{y}_{n0}{}^{(k)}) +\mathbf{R}_k\cdot(\mathfrak{y}_{n0}{}^{(i)}\times\mathfrak{y}_{0n}{}^{(k)})], \quad (24)$$

$$g^{(1)}=\frac{c}{6\pi ih}\sum_{i\neq k=1}^{N+1}\sum_n{}'\frac{\mathbf{m}_{0n}{}^{(k)}\cdot\mathfrak{y}_{n0}{}^{(i)}-\mathbf{m}_{n0}{}^{(k)}\cdot\mathfrak{y}_{0n}{}^{(i)}}{\nu_{n0}^2-\nu^2},$$

where g_k is the internal rotatory parameter of group k, itself. In simple optically active compounds the g_k vanish. If the retardation of the electromagnetic wave over all parts of each group is approximated by its value at the center of gravity of the group, $g^{(1)}$ vanishes, and the rotatory parameter reduces to $g^{(0)}$. We shall make this approximation in the present article, remarking that it is common to all previous theories of optical activity based upon localized oscillators.

For the calculation of $g^{(0)}$, we start with approximate molecular wave functions $\psi_n{}^0$, which are the eigenfunctions of a Hamiltonian including the interactions of the subsidiary groups with the central group, but not the interactions of the subsidiary groups among themselves. Because of the interaction between the subsidiary groups the wave functions will undergo a perturbation. We suppose that the subsidiary groups are sufficiently distant from each other that it is sufficient to retain only the dipole term in the potential, V, of their interaction

$$V=\sum_{i>j=1}^{N}\mathfrak{y}^{(i)}\cdot\mathbf{T}_{ji}\cdot\mathfrak{y}^{(j)},$$
$$\mathbf{T}_{ji}=\frac{1}{R_{ji}{}^3}\left[1-3\frac{\mathbf{R}_{ji}\mathbf{R}_{ji}}{R_{ji}{}^2}\right]. \tag{25}$$

The use of this potential, of course, requires the neglect of electron exchange between the subsidiary groups. If any of the states n are degenerate, we select for the corresponding $\psi_n{}^0$, a set of linear combinations of the eigenfunctions of the degenerate state, which diagonalize V. This can in general be done with real linear combinations and it will be convenient to have all the $\psi_n{}^0$ real in subsequent calculations.

The spectrum associated with the approximate wave functions $\psi_n{}^0$ is, of course, not the actual spectrum of the molecule, since the mutual perturbation of the secondary groups has been neglected. However, in the absence of structural resonance the two spectra will not be expected to differ much. Thus the spectrum of an organic radical retains to a large extent its identity in different compounds of which it is a substituent and is influenced considerably only by groups which are its nearest neighbors, in this case the central group. The approximate additivity of atomic refractions and atomic volumes of organic compounds are related to this fact. Moveover, for the same reasons, the zero-order spectrum can be characterized by sets of quantum numbers $n_1,\ n_2\cdots n_{N+1}$ associated with the individual groups of the molecule, corresponding to a set of normalized orthogonal wave functions, $\psi_n{}^0=\psi^0{}_{n_1,\ n_2\ldots n_{N+1}}$ with the following property

$$[f(q_i)]_{n'n}=[f(q_i)]_{n_i'n_i}\prod_{l\neq i=1}^{N+1}\delta_{n_l'n_l}, \tag{26}$$

where $f(q_i)$ is any function of the coordinates, q_i, of the electrons of group i alone. This amounts to assuming that the wave functions, $\psi_n{}^0$, can be expressed in the form, $\prod_{i=1}^{N+1}\varphi_{n_i}(q_i)$, where $\varphi_{n_i}(q_i)$ depends only on the coordinates of the electrons of group i. The function $\varphi_{n_i}(q_i)$ may be regarded as a generalized "self-consistent field" function of group i as a whole in the presence of the central group. Thus exchange between the subsidiary groups and the central group is really neglected. Accordingly the above wave functions would be poor in the neighborhood of the valence bonds and quite unsuitable for the calculation of bond energies. However, since the number of bonding electrons between the central group and the subsidiary groups is small in comparison with the total number of electrons in the molecule, these wave functions should be adequate for the calculation of the optical properties of the molecule, unless the bonding electrons make abnormally large contributions. It is to be remarked that electron exchange within the groups themselves is not neglected. The perturbation of the wave functions of the molecule resulting from the mutual interaction of the subsidiary groups may be calculated by the usual methods. The perturbed wave functions $\psi_{n_1,\ n_2,\ldots n_{N+1}}$ may be written to the first order in the following form when use is made of Eqs. (25) and (26).

$$\psi_{n_1\ldots n_{N+1}}=\psi^0{}_{n_1\cdots n_{N+1}}-\frac{1}{h}\sum_{i>j=1}^{N}\sum_{n'_in'_j}{}'\times\frac{(V_{ji})_{n_j'n_l';\ n_jn_l}\psi_{n_1}{}^0{}_{\ldots n_j'\ldots n_l'\ldots n_{N+1}}}{\nu_{n_j'n_j}+\nu_{n_j'n_l}}. \tag{27}$$

Calculation of $\mathfrak{y}_{n0}{}^{(i)}\times\mathfrak{y}_{n0}{}^{(k)}$ with these wave functions leads to the result,

$$\mathfrak{y}_{0n}{}^{(i)}\times\mathfrak{y}_{r0}{}^{(k)}=$$

$$-\frac{1}{h}\sum_{n_k'}{}'\left\{\frac{(V_{ik})_{n_i0;\,0n_k'}(\mathfrak{y}^{(i)}{}_{0n_i}\times\mathfrak{y}^{(k)}{}_{n_k'0})}{\nu_{n_k'0}-\nu_{n_i0}}\right.$$

$$\left.+\frac{(V_{ik})_{n_in_k';\,00}(\mathfrak{y}^{(i)}{}_{0n_i}\times\mathfrak{y}^{(k)}{}_{0n_k'})}{\nu_{n_k'0}+\nu_{n_i0}}\right\}\prod_{l=1\neq i}^{N+1}\delta_{n_l0} \qquad (28)$$

$$-\frac{1}{h}\sum_{n_i'}{}'\left\{\frac{(V_{ik})_{n_i'0;\,0n_k}(\mathfrak{y}^{(i)}{}_{0n_i'}\times\mathfrak{y}^{(k)}{}_{n_k0})}{\nu_{n_i'0}-\nu_{n_k0}}\right.$$

$$\left.+\frac{(V_{ik})_{00;\,n_i'n_k}(\mathfrak{y}^{(i)}{}_{n_i'0}\times\mathfrak{y}^{(k)}{}_{n_k0})}{\nu_{n_i'0}+\nu_{n_k0}}\right\}\prod_{l=1\neq k}^{N+1}\delta_{n_l0}.$$

With the wave functions (27), the sum in Eq. (24), defining $g^{(0)}$, of course, becomes a multiple sum over n_1, n_2, $\cdots n_{N+1}$ and ν_{n0} becomes $\nu_{n_10}+\nu_{n_20}+\cdots\nu_{n_{N+1}0}$, where ν_{n_i0} is a frequency of group i. Substituting Eq. (28) in Eq. (24), and making use of the fact that all $\mathfrak{y}_{n0}{}^{(i)}$ are real and thus equal to $\mathfrak{y}_{0n}{}^{(i)}$, since the $\psi_n{}^0$ have been chosen real, we obtain after some algebraic simplification

$$g^{(0)}=-\frac{2}{3h^2}\sum_{i\neq k=1}^{N}\sum_{n_i}{}'\sum_{n_k}{}' \qquad (29)$$

$$\times\frac{\nu_{n_i0}\nu_{n_k0}(\mathfrak{y}^{(i)}{}_{n_i0}\cdot\mathbf{T}_{ik}\cdot\mathfrak{y}^{(k)}{}_{n_k0})\mathbf{R}_k\cdot(\mathfrak{y}^{(i)}{}_{n_i0}\times\mathfrak{y}^{(k)}{}_{n_k0})}{(\nu^2{}_{n_i0}-\nu^2)(\nu^2{}_{r_k0}-\nu^2)}.$$

Actually the initial substitution of (28) in (24) yields two sums, one over n_i and n_k' and one over n_i' and n_k. Since the labeling is entirely arbitrary, both are relabeled as sums over n_i and n_k, and combined. We remark that the polarizability tensor of group i has the form

$$\boldsymbol{\alpha}^{(i)}=\frac{2}{h}\sum_{n_i}{}'\frac{\nu_{n_i0}\mathfrak{y}^{(i)}{}_{n_i0}\mathfrak{y}^{(i)}{}_{n_i0}}{\nu^2{}_{n_i0}-\nu^2}, \qquad (30)$$

so that we may write

$$\boldsymbol{\alpha}^{(i)}\mathbf{T}_{ik}\cdot\boldsymbol{\alpha}^{(k)}=\frac{4}{h^2}\sum_{n_i}{}'\sum_{n_k}{}'$$

$$\times\frac{\nu_{n_i0}\nu_{n_k0}(\mathfrak{y}^{(i)}{}_{n_i0}\cdot\mathbf{T}_{ik}\cdot\mathfrak{y}^{(k)}{}_{n_k0})\mathfrak{y}^{(i)}{}_{n_i0}\mathfrak{y}^{(k)}{}_{n_k0}}{(\nu^2{}_{n_i0}-\nu^2)(\nu^2{}_{n_k0}-\nu^2)}. \qquad (31)$$

From Eqs. (16), (29) and (31), we see that $g^{(0)}$ may be expressed in the following form

$$g^{(0)}=-\sum_{i\neq k=1}^{N}((\mathbf{a}_3\cdot\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}\cdot\boldsymbol{\alpha}^{(k)}\cdot\mathbf{a}_2)(\mathbf{R}_k\cdot\mathbf{a}_1))_{Av}, \qquad (32)$$

a formula which allows the calculation of $g^{(0)}$ from the polarizability tensors of the subsidiary groups and the geometry of the molecule. Eq. (32) would have been the first term in Boys' polarizability theory, had he not assumed the groups to be optically isotropic. By a very tedious extension of the perturbation calculation, the next approximation of the polarizability theory, considered by de Mallemann, involving sets of three groups has been verified, although small additional terms connected with frequency shifts caused by the perturbation appear. The Boys term would appear only if third-order terms were included in the perturbed wave function (27). If the groups are optically isotropic, the Boys term is the first one which does not vanish. Although the anisotropy of the groups might introduce only a moderate correction to the Boys term itself, it cannot be neglected for it enters into a much earlier approximation. It is our opinion that the Boys term and the one preceding it are seldom very important in comparison with the initial term in the polarizability theory given by Eq. (32). This will be substantiated by calculations based upon reasonable assumptions as to the geometry of the active molecule. Nevertheless, we see that the polarizability theory is correct in principle, since it can be obtained from Born's quantum-mechanical theory with not unreasonable methods of approximation. Unless the bonding electrons between the central group and the subsidiary groups make disproportionately large contributions to the optical rotatory power, which does not seem likely, the polarizability theory should be adequate as a good first approximation.

Let us suppose that $\mathbf{b}_1{}^{(i)}$, $\mathbf{b}_2{}^{(i)}$, $\mathbf{b}_3{}^{(i)}$ are unit vectors defining the principal optical axes of group i and $\mathbf{b}_1{}^{(k)}$, $\mathbf{b}_2{}^{(k)}$, $\mathbf{b}_3{}^{(k)}$ a set of vectors specifying those of group k. Then from Eqs. (16) and either (29) or (32), $g^{(0)}$ may be expressed as follows.

$$g^{(0)}=-\frac{1}{6}\sum_{i\neq k=1}^{N}\sum_{r,\,s=1}^{3}\alpha_{rr}{}^{(i)}\alpha_{ss}{}^{(k)}$$

$$\times(\mathbf{b}_r{}^{(i)}\cdot\mathbf{T}_{ik}\cdot\mathbf{b}_s{}^{(k)})\mathbf{R}_k\cdot(\mathbf{b}_r{}^{(i)}\times\mathbf{b}_s{}^{(k)}), \qquad (33)$$

where $\alpha_{rr}^{(i)}$ and $\alpha_{ss}^{(k)}$ are the elements of the diagonalized polarizability tensors of the two groups. If each group possesses an optical axis of symmetry, the formula may be simplified. We may designate the symmetry axes of the two groups i and k by unit vectors, $\mathbf{b}_i$ and $\mathbf{b}_k$. The polarizability tensor of group i may be written in the form

$$\boldsymbol{\alpha}^{(i)}=\alpha_i[(1-\beta_i/3)+\beta_i\mathbf{b}_i\mathbf{b}_i],$$

$$\beta_i=\frac{\alpha_{11}^{(i)}-\alpha_{22}^{(i)}}{\alpha_i}=3\frac{\alpha_{11}^{(i)}-\alpha_{22}^{(i)}}{\alpha_{11}^{(i)}+2\alpha_{22}^{(i)}}, \tag{34}$$

where α_i is the mean polarizability of group i and $\alpha_{11}^{(i)}$ and $\alpha_{22}^{(i)}$ are the components of $\boldsymbol{\alpha}^{(i)}$ parallel and perpendicular to $\mathbf{b}_i$. After some algebraic simplification the averaging process indicated in Eq. (32) yields with the use of polarizability tensors of the above form

$$g^{(0)}=-\frac{1}{6}\sum_{i>k=1}^{N}\alpha_i\alpha_k\beta_i\beta_kG_{ik}\mathbf{R}_{ik}\cdot(\mathbf{b}_i\times\mathbf{b}_k), \tag{35}$$

$$G_{ik}=\mathbf{b}_i\cdot\mathbf{T}_{ik}\cdot\mathbf{b}_k=\frac{1}{R_{ik}^3}\left[\mathbf{b}_i\mathbf{b}_k-3\frac{(\mathbf{b}_i\cdot\mathbf{R}_{ik})(\mathbf{b}_k\cdot\mathbf{R}_{ik})}{R_{ik}^2}\right],$$

$$\mathbf{R}_{ik}=\mathbf{R}_k-\mathbf{R}_i,$$

where the sum includes each pair of groups only once, as indicated by the notation $i>k$. Each term in $g^{(0)}$ vanishes not only if either group is isotropic but also if $\mathbf{b}_i$ and $\mathbf{b}_k$ are coplanar, since in the latter case the three vectors $\mathbf{R}_{ik}$, $\mathbf{b}_i$ and $\mathbf{b}_k$ are coplanar and the triple vector product vanishes. Thus any pair of groups, i and k, with optical axes of symmetry parallel to the respective bonds linking them to an asymmetric carbon atom, make no contribution to $g^{(0)}$. Such symmetry would result if there were free rotation of polyatomic groups about the bonds linking them to an asymmetric carbon atom, and it would be necessary to seek the rotatory power of the group in the next approximation of the polarizability theory, which is usually very small. However, by means of an hypothesis about restricted rotation, we shall see that $g^{(0)}$ cannot be expected to vanish. We suppose that the ground electronic state of the molecule comprises a number of torsional vibrational states, v, associated with rotation around the valence bonds between the subsidiary groups and the central group. Some of these states may be degenerate and some closely spaced relative to kT, the product of Boltzmann's constant and the absolute temperature. The parameter $g^{(0)}$ for the molecule will then be the average value of the $g_v^{(0)}$ of these states

$$g^{(0)}=\frac{\sum_v g_v^{(0)}e^{-E_v/kT}}{\sum_v e^{-E_v/kT}}, \tag{36}$$

where E_v is the energy of state, v, referred to the lowest of the states as zero. In particular if there are n equivalent sharp minima in the potential function associated with the relative orientations of the groups, permitted by rotation about the bonds linking them to the central group, while all other minima are higher by an energy difference large relative to kT, $g^{(0)}$ may be approximately calculated by the formula

$$g^{(0)}=\frac{1}{n}\sum_{n=1}^{n}g_r^{(0)}, \tag{37}$$

where $g_r^{(0)}$ is to be calculated from Eq. (35) for the orientation r and the sum extends over all orientations of equal potential energy. This formula implies that the amplitude of vibration in lowest vibrational state of each minimum is so small that fluctuations in the orientations can be neglected. We shall presently employ this formula in the calculation of $g^{(0)}$ for simple optically active molecules. As an illustration let us consider secondary butylalcohol. We tentatively assume that due to van der Waals forces and polarization forces, there are two orientations of equal energy for the C−C bond of the ethyl group, which makes a tetrahedral angle with the bond to the asymmetric carbon atom, C*. In one of these, the axis of the ethyl group is coplanar with the C*−OH bond and in the other with the C*−CH_3 bond. The third possible orientation in which the axis is coplanar with the C*−H bond is supposed to correspond to a minimum higher than the other two by an energy fairly large relative to kT. If this orientation had a probability equal to that of the other, $g^{(0)}$ would vanish. These assumptions are entirely reasonable in the light of recent evidence[15] relative to restricted rotation in ethane itself. Due probably

[15] Kemp and Pitzer, J. Am. Chem. 59, 276 (1937).

to van der Waals forces between the hydrogen atoms, there appear to be three equivalent relative orientations of the methyl groups, separated by energy barriers greater than 3000 cal. When some of the hydrogens of each methyl group are replaced by larger radicals with greater capacity for van der Waals attraction than hydrogen, not only would the sharpness of the minima be enhanced, but also differences in depth large relative to kT at ordinary temperatures could be expected.

Some general remarks about the equations of the present theory are perhaps appropriate at this point. The rotatory parameter may be written in the form

$$g=\frac{e^2}{m}\sum_n{}'\frac{g_{n0}}{\nu_{n0}^2-\nu^2}, \tag{38}$$

where the g_{n0} satisfy the following sum rule according to the general theory of Born.[5, 10]

$$\sum_n{}'g_{n0}=0. \tag{39}$$

It may be readily verified by use of familiar commutation rules that the approximate $g_{n0}^{(0)}$ entering into the expression for $g^{(0)}$ of Eq. (24) satisfy the sum rule (39). Thus the polarizability theory is in accord with the general theory in this respect. The use of Eq. (29) with appropriate modification to allow for radiation damping, is not to be recommended in the immediate neighborhood of an absorption band of the molecule, because of the likelihood of poor convergence of the perturbation calculation under these conditions. However, the Cotton effect, involving a change in sign of the parameter g in the neighborhood of an absorption band, can be qualitatively understood from Eqs. (29), (33) and (35). The absorption frequencies associated with different components of the polarizability tensor of a group will in general have different selection rules. It is easy to see that these selection rules could operate to produce a change in sign in one or more of the constants β_i of Eqs. (34) and (35), with a resultant change of sign in $g^{(0)}$ when certain absorption bands are traversed. Objection[8, 9] has been raised to the polarizability theories of de Mallemann, Gray and Boys on the ground that measurements of circular dichroism show that the major contributions to the rotatory parameter g generally come from relatively weak absorption bands of the molecule, whereas the major contributions to the polarizability of the molecule as a whole, come from the strongest bands. This objection seems untenable as far as the general polarizability theory is concerned, for several reasons. In the first place, a large part of the existent data on circular dichroism refers to complicated molecules and is difficult to interpret from the standpoint of structure. It may very well happen that the strongest absorption bands are associated with groups which do not contribute to the sum of Eq. (35) because of unfavorable orientation of their optical axes relative to those of other groups in the molecule. In the second place, there is nothing in the polarizability theory which requires the g_{n0} of Eq. (24) to be proportional to the f_{n0}, the corresponding dispersion f values of the molecule. The f_{n0} of the molecule as a whole involve sums of the f values of its constituent groups, while the g_{n0} values, according to the polarizability theory, involve products of the f values of the groups. From Eq. (29), it is evident that overlapping regions in the absorption bands of the zero-order spectra of two groups might well make the most important contributions to the rotatory parameter.[16] Although no general statement can be made, there is no reason to suppose that such overlapping ordinarily occurs in the absorption bands of maximum intensity for two groups of different structure.

III

In order to apply the present theory, it is necessary to have information about the polarizability tensors, $\boldsymbol{\alpha}^{(i)}$, of the groups constituting an active molecule. The mean polarizability, α_i, equal to one-third the diagonal sum of $\boldsymbol{\alpha}^{(i)}$, may be estimated from the atomic refractions, A_s, of the atoms constituting the group by means of the formula,

$$\alpha_i=\frac{3}{4\pi N}\sum_s{}^{(i)}A_s, \tag{40}$$

where the sum extends over all atoms of the

[16] Degeneracy arising from such overlapping has been taken care of in the perturbation calculation by choosing for the Ψ_n^0, linear combinations which diagonalize V.

group.[17] The determination of the anisotropy ratios, β_i, defined by Eq. (34), and the relative orientation of the optical axes of the subsidiary groups in an active molecule is considerably more difficult. The polarizability tensors entering into Eq. (35) for $g^{(0)}$ are calculated with a wave function which includes the interaction of each subsidiary group with the central group, but not the mutual interaction of the subsidiary groups themselves. When the central group is an asymmetric carbon atom, it is reasonable to estimate the anisotropy induced in a subsidiary group R by the central group from a study of the optical properties of the compound RCH_3. In the case of a polyatomic group with intrinsic anisotropy, the properties of the compound RH may also be used. For this purpose, we shall turn to measurements of the degree of depolarization of light scattered by the vapors of the compounds RCH_3 and RH at an angle of 90° to the incident beam. The Kerr effect also furnishes information about molecular anisotropy, but there are few data on the vapors of nonpolar substances, and its interpretation in the case of polar substances is complicated by the role of the permanent dipole moment.

The principal polarizabilities of a molecule, α_{11}, α_{22}, and α_{33} are related to the degree of depolarization,[18] Δ, of light scattered by the vapor, in the following manner.

$$[(\alpha_{11}-\alpha_{22})^2+(\alpha_{11}-\alpha_{33})^2+(\alpha_{22}-\alpha_{33})^2]/\alpha^2 = 90\Delta/(6-7\Delta), \quad (41)$$

$$\alpha=\tfrac{1}{3}[\alpha_{11}+\alpha_{22}+\alpha_{33}].$$

We may define a general anisotropy ratio β by the relation.

$$\beta^2=[(\alpha_{11}-\alpha_{22})^2+(\alpha_{11}-\alpha_{33})^2+(\alpha_{22}-\alpha_{33})^2]/2\alpha^2,$$

$$\beta=\pm(45\Delta/(6-7\Delta))^{\frac{1}{2}}. \quad (42)$$

When the molecule possesses an optical axis of symmetry, $\alpha_{22}=\alpha_{33}$, the above definition of β becomes identical with that of Eq. (34), employed for the groups of an active molecule. The positive or negative sign is to be taken according to whether the polarization ellipsoid is prolate or oblate.

TABLE I.

	$\alpha\cdot10^{24}$(cc)	β
CH_3	2.25	0.35
C_2H_5	4.07	.35
OH	1.03	.35
Cl	2.35	.35
NH_2	1.78	.25*
COOH	2.86	.55
C_6H_5	9.89	−.58

Although we shall not attempt to develop a molecular theory of anisotropy at the present time, we shall suppose, for purposes of approximation, that in a molecule consisting of two groups, not only the mean polarizability but also each component of its polarizability tensor may be expressed as the sum of the corresponding components of polarizability tensors of the two groups, referred to a common set of axes. If the groups have a common axis of symmetry, directed along the bond between them, the anisotropy ratio, β, of the molecule may be expressed in the form $(\alpha_1\beta_1+\alpha_2\beta_2)/(\alpha_1+\alpha_2)$, where α_1, α_2, β_1 and β_2 are the mean polarizabilities and anisotropy ratios of the respective groups. Although the anisotropy ratio of each group may be expected to depend somewhat upon the nature of the other, we shall arbitrarily assume that CH_3 has the same anisotropy ratio in different compounds CH_3R in which R is a monatomic group or a simple polyatomic group. From the degree of depolarization, Δ, of ethane, 0.016, we calculate a value of β equal to 0.35. According to the above considerations this is also the anisotropy ratio of one methyl group in the presence of another. The compounds CH_3OH and CH_3Cl have values of Δ equal to 0.016 and 0.015, respectively. Assuming the anisotropy ratio of CH_3 to be the same in these compounds as in C_2H_6, we assign a value of β equal to 0.35 to both OH and Cl, bonded to carbon. It is of course questionable to treat the group OH in methylalcohol as having an axis of symmetry along the C−O bond, although this will be true on the average, since the O−H can doubtless assume three equivalent positions with respect to the three C−H bonds in the methyl group. In the case of polyatomic groups, the anisotropy of which may be expected to be largely internally

[17] Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, Hw. II, 985; Eisenlohr, Zeits. f. physik. Chemie **75**, 585 (1910); **79**, 129 (1912).

[18] Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, Eg II*a* 88; Eg III, 1204.

determined, we make use of the compounds RH. From formic acid, $\Delta=0.038$, we obtain a value of β equal to 0.55 for the carboxyl group. As a rough approximation the carboxyl group may be treated as having an axis of symmetry parallel to a vector joining the oxygen atoms, since the polarizability along this axis doubtless differs from either of the two polarizabilities in a plane perpendicular to it by an amount considerably greater than their own difference. From benzene, $\Delta=0.042$, a value of β for the phenyl group of -0.58 is obtained. This value is in substantial agreement with that obtained from measurements of the Kerr effect in benzene vapor.[19] The mean polarizabilities and the anisotropy ratios, estimated in the manner described, for several common organic groups are listed in Table I. The value of β for NH_2 obtained from the degree of depolarization of methylamine is 0.11. Since the compound has been measured by only one investigator and 0.11 seems rather too low, the value 0.25 is suggested as more probable. Although structural resonance is present in the group COOH and C_6H_5, the present theory of rotatory power may be applied to compounds containing these groups, providing their structure is such that resonance cannot extend outside these groups. The estimates of the anisotropy ratios given in Table I are admittedly rough and subject to revision, for not only is the method of calculation rather crude, but also the measurements of depolarization are very sensitive to error. Nevertheless, we believe that they are of the correct magnitude.

For the calculation of the functions G_{ik} in Eq. (35), it is necessary to know the configuration of the active molecule and its dimensions. For this purpose we use the atomic radii tabulated by Pauling and Huggins.[20] The most important interatomic distances are C−C, 1.54A; C=C, 1.38A; C−N, 1.47A, and C−O, 1.43A. These distances together with the trigonometric functions of the tetrahedral angle suffice to characterize the geometry of a number of simple organic molecules.

We shall not undertake a systematic calculation of optical rotation in the present article, but we shall illustrate the application of Eqs. (35) and (37) in the case of secondary butyl-alcohol. The central group is here an asymmetric carbon atom C* and the subsidiary groups are H, OH, CH_3, and C_2H_5. We suppose that the groups H, OH, and CH_3 have optical axes of symmetry directed along their bonds to C*. Because of its small size and polarizability and since the C−H bond is somewhat polar, it would probably be better to treat H as a part of the central group. In the present case we shall see that it does not contribute directly to the rotatory parameter. We could assign to the ethyl group an optical axis directed along the C−C bond as in ethane. However, the central group, C*, might be expected to tilt the optical axis (not the geometrical axis) of the ethyl group toward itself. There is evidence in the degree of depolarization of propane for an effect of this sort. A reasonable assignment of the optical axis would be to place it in the plane of C* and the C−C bond of the ethyl inclined at one-half the tetrahedral angle to the C−C bond. As outlined in an earlier section we assume two orientations of the ethyl group of equal probability, in which the C−C bond of the ethyl group is coplanar with the C*−OH and with the C*−CH_3 bonds, respectively. We shall designate these orientations as *a* and *b*. The third possible orientation beneath the C−H bond is assumed to be of negligible probability because of a small Boltzmann factor. This does not mean that there is not free rotation of the ethyl group through this position in the sense of the organic chemist's use of the term since the potential barriers hindering the rotation of the ethyl group doubtless correspond to low activation energies.

From Eq. (35) we see that the mutual interaction of the three groups H, OH, and CH_3 cannot contribute to the rotatory parameter since the optical axes of each pair terminate in C* and are therefore coplanar with the corresponding $\mathbf{R}_{ik}$. Moreover, no contribution can arise from the interaction of the groups C_2H_5 and H, if the ethyl group has two equivalent orientations beneath the C−CH_3 and C−OH bonds, since $\mathbf{R}_{ik}\cdot(\mathbf{b}_i\times\mathbf{b}_k)$ merely changes sign in passing from position *a* to position *b* and all other factors remain the same, with a resultant cancellation of the contributions from the two

[19] H. A. Stuart, *Molekülstruktur* (Berlin, 1934), p. 173.
[20] Pauling and Huggins, Zeits. f. Krist. **87**, 205 (1934).

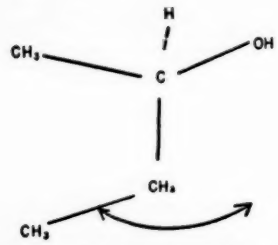

FIG. 1. Configuration of *d*-secondary butyl alcohol. The hydrogen atom bonded to the asymmetric carbon is behind the plane of the paper.

positions. In position *a*, the only other non-vanishing term in $g^{(0)}$ arises from the groups C_2H_5 and CH_3, while in position *b*, the only other contribution arises from the groups C_2H_5 and OH. If we designate the values of $g^{(0)}$ in the two positions by $g_a{}^{(0)}$ and $g_b{}^{(0)}$ (omitting for simplicity the canceling terms for H), the mean rotatory parameter of the molecule may be expressed in the form,

$$\begin{aligned}(g^{(0)})_{Av}&=\tfrac{1}{2}(g_a{}^{(0)}+g_b{}^{(0)}),\\ g_a{}^{(0)}&=-\tfrac{1}{6}\alpha_1\alpha_2\beta_1\beta_2 G_{12}\mathbf{R}_{12}\cdot(\mathbf{b}_1\times\mathbf{b}_2),\\ g_b{}^{(0)}&=-\tfrac{1}{6}\alpha_1\alpha_3\beta_1\beta_3 G_{13}\mathbf{R}_{13}\cdot(\mathbf{b}_1\times\mathbf{b}_3),\end{aligned}\qquad(43)$$

where the subscripts 1, 2, and 3 in the expressions for $g_a{}^{(0)}$ and $g_b{}^{(0)}$ refer to the groups ethyl, methyl, and hydroxyl, respectively. The distances C*−CH_3, and C*−OH are taken as 1.54A and 1.43A, respectively, and the center of the ethyl group is located at the midpoint of its C−C bond, a distance of 0.77A from either carbon. The distance of the asymmetric carbon atom from the ethyl carbon to which it is bonded is 1.54A. The bond angles are all taken as the tetrahedral angle, 109° 28′. These data suffice to fix the configuration of the groups in the two orientations, *a* and *b*, and allow the calculation of G_{12}, G_{13}, $\mathbf{R}_{12}\cdot(\mathbf{b}_1\times\mathbf{b}_2)$, and $\mathbf{R}_{13}\cdot(\mathbf{b}_1\times\mathbf{b}_3)$ once we have fixed the optical axis $\mathbf{b}_1$ of the ethyl group. We shall first assume it to be directed along the C−C bond. For the dextro configuration, Fig. 1, in which the groups CH_3, OH, and H appear in clockwise order when the molecule is viewed with the ethyl group toward the observer, the following values of $g_a{}^{(0)}$, $g_b{}^{(0)}$, and $(g^{(0)})_{Av}$ are obtained

$$\begin{aligned}g_a{}^{(0)}&=9.88\times10^{-3}A^4,\\ g_b{}^{(0)}&=-4.86\times10^{-3},\\ (g^0)_{Av}&=+2.51\times10^{-3}.\end{aligned}\qquad(44)$$

When the optical axis $\mathbf{b}_1$ of the ethyl group is tilted to an angle of 54° 44′ with the C−C bond, remaining in the plane of this bond and the C*−C_2H_5 bond, the dextro configuration remains unchanged, but somewhat different values of $g^{(0)}$ are obtained

$$\begin{aligned}g_a{}^{(0)}&=4.26\times10^{-3}A^4,\\ g_b{}^{(0)}&=-2.12\times10^{-3},\\ (g^{(0)})_{Av}&=1.07\times10^{-3}.\end{aligned}\qquad(45)$$

The refractive index of pure secondary butylalcohol corresponds to a value of $(n^2+2)/3$ of 1.32 at 20°C. Substitution of the values of $(g^{(0)})_{Av}$ calculated above, into Eq. (8) leads to the following values for the specific rotation of *d*-secondary butylalcohol.

$$\begin{aligned}[\alpha]_D{}^{20}&=21.9^\circ\quad(g=2.51\times10^{-3})\\ &=\ 9.5^\circ\quad(g=1.07\times10^{-3})\\ &=13.9^\circ\quad(\text{observed}).\end{aligned}$$

The observed rotation[21] lies between the values corresponding to the two extreme orientations of the optical axis of the ethyl group. The calculated values are definitely of the correct magnitude, although their numerical values might be shifted somewhat by small changes in the relative distribution of the ethyl group between positions *a* and *b* and by small reorientations of the optical axes of the groups. Probably the most serious defect in the calculation lies in the treatment of the hydroxyl group as axially

[21] To meet the possible objection that the rotatory power of pure secondary butylalcohol might be materially influenced by intermolecular interaction through the alcoholic hydroxyl groups, we call attention to the fact $3[\alpha]_D{}^{20°}/(n^2+2)$ has approximately the same value in the pure alcohol as in its solutions in benzene and carbon disulfide. (Pickard and Kenyon, J. Chem. Soc. **105**, 883 (1914).)

d-secondary butylalcohol

Solvent	$[3/(n^2+2)]\,[\alpha]_D{}^{20°}$
pure alcohol	10.4°
benzene	10.3
carbon disulfide	11.1

The assumption that in secondary butylalcohol the two orientations of the ethyl group, below the hydroxyl group and below the methyl group, are of about equal probability is entirely reasonable. The van der Waals energy of the ethyl group and the methyl group is doubtless a little greater than that of the ethyl group and hydroxyl. However, this difference will tend to be compensated by the energy of polarization of the ethyl group by the hydroxyl dipole and by the fact that the minimum distance between the ethyl and hydroxyl groups is a little smaller than that between the ethyl and methyl groups. It is interesting to remark that an abnormally strong interaction between the ethyl and hydroxyl group, fixing the ethyl group beneath the hydroxyl would leave the proposed absolute configuration of *d*-secondary butylalcohol unchanged, but would lead to far too high a value of $[\alpha]_D{}^{20°}$ unless the optical axes of the groups were reoriented.

symmetric relative to the C−O bond, since the hydroxyl hydrogen may produce some anisotropy in the plane perpendicular to this bond. Whether this is an important effect must await subsequent calculations. The absolute configuration of *d*-secondary butylalcohol shown in Fig. 1 must be regarded as tentative for these reasons, but it is probably correct.

The next approximation in the polarizability theory has not been calculated, but the third approximation has been estimated from Boys' formula,[3] with the center of the ethyl group fixed on the $C^*-C_2H_5$ bond at a distance of 2.17A from the asymmetric carbon atom, a position which is actually its projection on this bond in any orientation. The carbon hydrogen distance is taken as 1.05A. The centers of the groups C_2H_5, CH_3, OH, and H are then situated at the vertices of a tetrahedron, the edges of which are approximately the pairwise sums of the distances 1.79; 1.25; 1.18; and 0.92A. With these dimensions the Boys term makes a contribution of less than 0.1° to $[\alpha]_D^{20°}$. Boys' term is very sensitive to the dimensions of the molecule. He himself obtained a much larger value for secondary butylalcohol, but with very improbable values for the inter-group distances. It is interesting to note, that both the present theory and that of Boys lead to the same absolute configuration for *d*-secondary butylalcohol. This will not always be the case, however, and it does not seem possible to predict absolute configurations by Boys' simple rule based upon the sizes of the substituent groups.

The example which has just been discussed serves to illustrate the possibilities of the present theory. At a later time a systematic application of the theory will be presented. The presence of inhibited rotation will generally be of considerable importance in determining the rotatory power of a molecule. It seems likely that it may be the key to an understanding of the dependence of rotatory power on temperature and upon the solvent in which the active molecule is dissolved.[22] From Eq. (36), the rotatory parameter would be expected to be sensitive to temperature if two or more orientations are associated with energies differing by an amount comparable with kT. Again a change of solvent could very well alter the probability distribution of a group among several possible orientations and so produce a marked change in the rotatory power of a molecule.

The present theory is, of course, crude in many respects and can never be expected to give more than a first approximation. A major improvement could be made if it were possible to avoid treating the electric moments induced in the groups of an active molecule as though they were localized at the centers of gravity. Moreover, we remark again that the theory may be expected to break down badly whenever there is structural resonance between groups.

Note added in Proof: It should be emphasized that the present theory is not limited by the special stereochemical model we have employed for secondary butylalcohol. Although the model is a plausible one, it is not entirely above reproach, because of the possibility of steric hindrance arising from repulsive forces between the groups. For this reason, we shall discuss two other models.

(1) Repulsive forces between the methyl groups make the *cis*-position, orientation (b), one of small probability. Under these conditions, it is reasonable to suppose that the potential energy has a minimum of appreciable depth only for orientation (a), in which the ethyl group lies beneath the hydroxyl group. The corresponding values of $[\alpha]_D^{20°}$ for the two orientations of the optical axis of the ethyl group are 86° and 38°. Neither value is in good agreement with the experimental rotation. The dextro configuration remains as shown in Fig. 1.

(2) Steric hindrance from both the methyl group and the hydroxyl group constrains the ethyl group to lie beneath the hydrogen, bonded to the asymmetric carbon. The corresponding values of $[\alpha]_D^{20°}$ are −44° and −19°. The latter value agrees fairly well with the rotation of the laevo alcohol. The absolute configuration is inverted and Fig. 1 represents the laevo form.

Our first model appears to give the best agreement with experiment and indeed seems to be the most probable one. On the other hand certain writers have suggested that steric hindrance may occur in compounds of the type of secondary butylalcohol. Thus Stuart, Phys. Rev. **38**, 1372 (1931), advances the view that in *n*-butane, the *cis*-position of the terminal methyl groups is one of small probability because of steric hindrance. However, his conclusion is based upon thermochemical evidence, the interpretation of which is not entirely unambiguous. From x-ray scattering experiments, Debye, Physik. Zeits. **31**, 142 (1930), concludes that 1,2-dichlorethane exists almost exclusively in the *trans* form. However, repulsive forces between the dipoles of the C−Cl bonds are sufficient to account for this fact.

It would be highly desirable to investigate the stereochemistry of secondary butylalcohol by the electron diffraction method. Once the most probable locations of the ethyl group are determined, the present theory of rotatory power can be applied without ambiguity.

[22] Beckmann and Cohen, J. Chem. Phys. **4**, 784 (1936).

On Transitions in Condensed Systems

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In this paper there is presented a method of studying transitions in condensed phases based on the thermodynamic equation $(\partial E/\partial V)_T = T(\partial S/\partial V)_T$, which holds for low pressures. $(\partial E/\partial V)_T$ and $T(\partial S/\partial V)_T$ are plotted as functions of V, the latter for various temperatures. Intersections of these curves give the points of equilibrium and the transition points. It is shown that very general and qualitative considerations, taking into account only facts that we definitely know to be true of these curves, with one very reasonable assumption, are sufficient to indicate that as the temperature of a system is increased from absolute zero there must be at least one change of phase, which is taken to be fusion. Changes of phase due to setting in of molecular rotation in the solid are also considered. Curves of N_2 and O_2 are constructed from available experimental data. Finally, an equation of Eyring and Hirschfelder, which would give the trend of the function $V(\partial S/\partial V)_T$ with V for liquids, is tested by a new method, and found not to accord very well with the experimental data, especially for low boiling substances.

§1. INTRODUCTION

RECENTLY a number of papers have appeared which deal with the theory of liquids and the nature of the transition between the liquid state and the solid state.[1] It is the purpose of the present communication to discuss these phenomena from a slightly different point of view, whose possibilities have not, so far as I am aware, been fully exploited. The method proposed is, we believe, of value because of the clear qualitative picture which it gives of the process of fusion and certain other types of transition. Further, it appears to be possible to predict, on extremely general premises, that on increasing the temperature from absolute zero, a condensed system must always go through at least one transition point, corresponding presumably to fusion. (At any rate, this is true if one can ignore the effect of vaporization, resulting in the possibility of sublimation, which nevertheless does not alter the fact that, as far as the *condensed* phase is concerned, at least one transition must occur.)

The essence of our procedure lies in the use of the thermodynamic equation

$$P+(\partial E/\partial V)_T = T(\partial S/\partial V)_T, \qquad (1)$$

where E is the molal energy, S the molal entropy, V the molal volume, and T the temperature of the system, and where P is the applied pressure.

In the case of solids and liquids at ordinary pressures P is negligible compared to $(\partial E/\partial V)_T$, so to determine the state of a solid or liquid, we may write the condition equation, which must be obeyed if $P=0$,

$$(\partial E/\partial V)_T = T(\partial S/\partial V)_T. \qquad (2)$$

One of the essential differences between equilibria involving only condensed phases at ordinary pressures and equilibria in which a vapor phase is present is that in the former case Eq. (2) may be used, but in the latter case Eq. (1) is necessary.

The condition (2) is just the condition that the free energy F (which is equal to $E-TS$ when $P=0$) should be a minimum or maximum. In order for the equilibrium to be stable F must be a minimum, or

$$(\partial^2 F/\partial V^2)_T = (\partial^2 E/\partial V^2)_T - T(\partial^2 S/\partial V^2)_T > 0. \qquad (3)$$

Let us now assume, what is no doubt not strictly true but can be used as an approximation (which is discussed in §3, below), that E and S can both be divided into two parts, one of which is a function of the temperature alone, and the other a function of the volume alone. This makes $(\partial E/\partial V)_T$ and $(\partial S/\partial V)_T$ functions only of V.

[1] See, for example, (*a*) Braunbeck, Zeits. f. Physik **99**, 259 (1936); (*b*) Kudar, Physik. Zeits. **35**, 560 (1934); (*c*) Franchetti, Atti Accad. Lincei **22**, 433, 585 (1935); (*d*) Herzfeld and Goeppert Mayer, Phys. Rev. **46**, 995 (1934); (*e*) Hill, Physik. Zeits. Sowjetunion **8**, 401 (1935); (*f*) Bijl, Physica **1**, 1125 (1934); (*g*) Frenkel, Acta Physicochim. U. S. S R. **3**, 633, 913 (1935); (*h*) Tarschisch, Zeits. f. Physik **99**, 259 (1936); (*i*) Mayer, J. Chem. Phys. **5**, 67 (1937); Mayer and Ackermann, ibid. **5**, 74 (1937); (*j*) Eyring and Hirschfelder, J. Phys. Chem. **41**, 249 (1937); (*k*) Rice, J. Chem. Phys. **5**, 353 (1937) (cited hereafter as I). For a general discussion of much of the recent work see (*l*) Trans. Faraday Soc. **33**, 1–104 (1937).

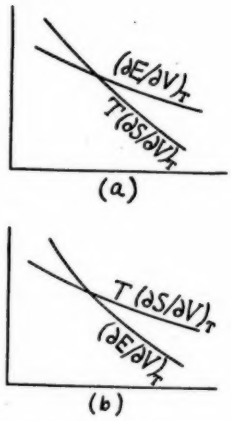

FIG. 1. Illustrating the types of intersection which can occur when $(\partial E/\partial V)_T$ and $T(\partial S/\partial V)_T$ are plotted as a function of the volume V; (a) represents a stable intersection (b) an unstable one.

Then Eq. (2) and the inequality (3) offer a convenient means of studying the changes of equilibrium as the temperature varies, and thus changes of phase such as occur on fusion. We simply plot out $(\partial E/\partial V)_T$ as a function of V, and on the same diagram $(\partial S/\partial V)_T$ multiplied by T, and note the points where these curves intersect. As T changes the curve $T(\partial S/\partial V)_T$ simply expands proportionately, and the series of intersections gives us all necessary information regarding the various changes of phase. The intersections of these curves give the points at which Eq. (2) holds. There are two kinds of possible intersections, as shown in Fig. 1. The type in which $(\partial E/\partial V)_T$ is below $T(\partial S/\partial V)_T$ to the left of the intersection, shown in 1(a) is, of course, the type for which (3) holds and hence represents a stable equilibrium.

§2. Equilibrium in Simple Liquids and Solids

We shall now consider the application of these principles to the case of solids and liquids in which the forces are of the van der Waals type. With this type of substance we can assume, at least as a first approximation, that if V is large enough $E=-a/V$, where a is a positive constant,[2] and thus

$$(\partial E/\partial V)_T=a/V^2. \tag{4}$$

[2] For very large volumes (i.e., for the gas phase) this van der Waals type correction holds for any substance, but for simple liquids it appears to hold approximately down into a part of the range of liquid volumes. See Hildebrand, *Solubility*, second edition (Reinhold Pub. Co., 1936) Chap. V. Setting E equal to the van der Waals correction, of course, simply amounts to taking the zero of energy at $V=\infty$.

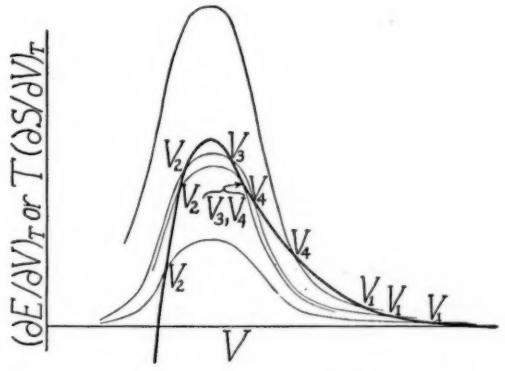

FIG. 2. Schematic curves illustrating the course of the phenomena of the condensed phase as the temperature is changed.

However, as the volume becomes smaller, and the average distance between molecules approaches the minimum of the potential curve for a pair of molecules, $(\partial E/\partial V)_T$ must reach a maximum and finally, at a volume such that most of the molecular pairs are practically at their equilibrium distance, pass through zero and become negative. The shape of the curve is illustrated in Fig. 2 (heavy curve). For S on the other hand, if V is sufficiently large, we have

$$(\partial S/\partial V)_T=R/V. \tag{5}$$

From the results [1(k)] of I we can make some attempt to evaluate $(\partial S/\partial V)_T$ for smaller volumes (around the boiling point of the liquid). We have defined an effective internal volume, V_e, by the equation $\Delta S=R\ln(V_v/V_e)$ where ΔS is the entropy of vaporization and V_v is the molal volume of the vapor, so that

$$(\partial S/\partial V)_T=RV_e^{-1}(\partial V_e/\partial V)_T. \tag{6}$$

Also, it has been shown that $(\partial V_e/\partial V)_T(V/V_e)$ is approximately 10 near the boiling point of the simple liquids considered. We thus see that for this range of volumes

$$(\partial S/\partial V)_T\sim 10R/V. \tag{7}$$

However, as we approach very small volumes, $(\partial S/\partial V)_T$ must eventually reach a maximum and return to zero, since the entropy must approach zero asymptotically as the volume is

decreased.[3] Thus $(\partial S/\partial V)_T$ will have the general shape shown by the light curves, $T(\partial S/\partial V)_T$, in Fig. 2. We make the assumption that the decrease in $(\partial S/\partial V)_T$ occurs in the range of volumes indicated.

These curves also indicate the course of the phenomena of the condensed state. At sufficiently low temperatures there will be an intersection at a large volume, in the region where Eqs. (4) and (5) both hold. The volume will be given by $V=a/RT$, and is thus inversely proportional to T. This point of intersection, which we shall designate as V_1, does not correspond to a state of stable equilibrium. There will, however, be a stable intersection very near the point at which the heavy curve crosses the axis if the temperature is very low. This occurs at a volume to be designated as V_2, and corresponds to the solid state. As the the temperature rises V_2 increases, as it should. When the temperature has risen sufficiently two more intersections appear, an unstable one at V_3 and a stable one at V_4, corresponding to the liquid state.[4] This happens because of the sharp rise in $(\partial S/\partial V)_T$ in going from the region where Eq. (5) holds to the region where Eq. (7) holds. The liquid, of course, does not become the most stable phase as soon as the intersection corresponding to it appears, but only when its free energy is less than that of the solid, which requires that

$$\int_{V_2}^{V_4}[(\partial E/\partial V)_T - T(\partial S/\partial V)_T]dV<0,$$

i.e., the area enclosed between the curves between the intersections at V_2 and V_3 must become less than that included between V_3 and V_4. Equality of these areas determines the melting point. As the temperature increases the intersections V_2 and V_3 finally coalesce and disappear as do V_4 and V_1. Which of these disappearances takes place first is not certain, but only the latter is of importance, and it corresponds roughly to the critical point.[5] We have thus been able to outline the behavior of solid and liquid from absolute zero to the critical point.

It will be clear that if the curves for $(\partial E/\partial V)_T$ and $(\partial S/\partial V)_T$ are known, various thermodynamic properties of solid and liquid may be readily calculated. In particular, the coefficient of expansion may be immediately deduced, since the diagram gives directly the equilibrium volume at any temperature. And the difference between the specific heat at constant volume, C_v, and that at constant pressure, C_p, can be calculated from the relation,

$$C_p-C_v=(\partial E/\partial V)_T(\partial V/\partial T)_P, \qquad (8)$$

which holds when $P=0$.

It is of interest to note that the intersection V_2, corresponding to the solid, will, unless the $(\partial S/\partial V)_T$ curve has a very peculiar shape, always be to the left of, or very near the maximum of the $(\partial E/\partial V)_T$ curve, while V_4 is always well to the right of the maximum.[6]

It is also of interest to remark that this analysis of the phenomena of the condensed phase appears to favor Frenkel's view that the transition between liquid and solid is a perfectly continuous one in the same sense that, according to van der Waals' theory, the transition between liquid and gas is continuous. Our treatment is similar to Frenkel's in that we consider the change of certain thermodynamic quantities with the volume, though he has considered only how the pressure varies as a function of volume for equilibrium states of the system. It is possible to construct Frenkel's P–V curve by holding T constant and letting the left-hand side of Eq. (1) vary with P, watching the intersections. Of course, part of Frenkel's curve corresponds to unstable equilibrium. This does not necessarily imply, however, that there will be a critical point for fusion like the critical point for vaporization;[7] this depends upon the respective shapes of the $P+(\partial E/\partial V)_T$ and $T(\partial S/\partial V)_T$ curves.

[3] See Lewis, Zeits. f. physik. Chemie **130**, 532 (1927).

[4] It is, of course, an assumption that this phase actually corresponds to the liquid state, since there is nothing in the theory to tell us about the fluidity of any phase. It remains true, however, that with this assumption the phenomena given by the theory can be brought into correspondence with those observed.

[5] The correspondence can only be rough, because P is not negligible compared to $(\partial E/\partial V)_T$ at the critical point.

[6] In the case of the metal mercury $(\partial E/\partial V)_T$ actually appears to be increasing with V for the liquid state. See Hildebrand, reference 2, p. 100.

[7] This matter has recently been discussed by Simon, reference 1 (*l*), pp. 65 ff.

§3. Limitations and Shortcomings of the Theory

One objection to the theory we have just outlined consists in the fact that the assumption, that $(\partial E/\partial V)_T$ and $(\partial S/\partial V)_T$ are functions of V and independent of the temperature, is undoubtedly not strictly correct. However, this may be corrected for by allowing the shape of the curves to gradually change as the temperature is changed, and it seems unlikely that the phenomena will be altered in any of their qualitative features. It is rather important to note that the asymptotic approach of $(\partial S/\partial V)_T$ to zero at small volumes will begin at a larger value of V the lower the temperature. Thus the value of V at which $(\partial E/\partial V)_T=0$ is already in the range of volumes for which $(\partial S/\partial V)_T=0$ when the temperature is near the absolute zero. At these temperatures, then, the volume remains practically stationary for a short temperature range, giving the necessary zero values for the coefficient of expansion and C_p-C_v. As the region where $(\partial S/\partial V)_T$ approaches zero pushes over toward smaller volumes the coefficient of expansion increases. $(\partial E/\partial V)_T$ is largely determined by the forces between the molecules, and its dependence on temperature should not be as important as that of $(\partial S/\partial V)_T$.

As Professor K. F. Herzfeld has remarked to me, it is easy to derive an expression for $(\partial S/\partial V)_T$ for a simple Debye solid, in the limiting region of very low temperatures or very low volumes. For in this region, according to the Debye theory, $S=(4/5)\pi^4R(T/\Theta)^3$, where Θ is the characteristic temperature. We have then $(\partial S/\partial V)_T=-(12/5)\pi^4R(T/\Theta)^3d\ \ln\ \Theta/dV$, whence it is seen that $(\partial S/\partial V)_T$ varies as T^3. On the other hand, in the classical region of high temperatures and large volumes $(\partial S/\partial V)_T$ will be expected to be independent of T.

Another difficulty with the picture we have presented rests in the fact that in the solid state S and E probably also depend to some extent on the arrangement of the molecules, as well as the actual volume they occupy. We thus need to introduce an "arrangement parameter." Some such parameter is necessary to account for some of the transitions between allotropic solid forms, which, however, would not be important for the picture in large outline.

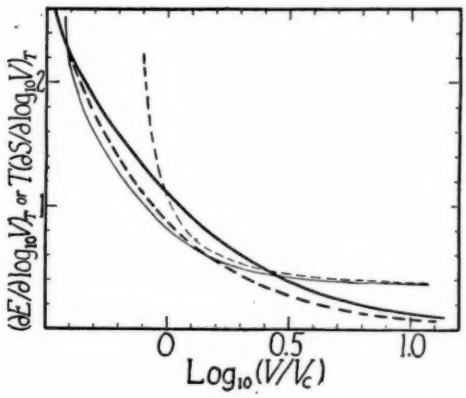

Fig. 3. Curves for N_2, large volumes. Heavy curve, $(\partial E/\partial \log V)_T$; heavy broken curve, approximation from Eq. (4); light curve $T(\partial S/\partial \log V)_T$; light broken curve, approximation from van der Waals' equation. The temperature for the $T(\partial S/\partial \log V)_T$ curves is 77.3°K, the boiling point of N_2. Energy units (for Figs. 3, 4, and 5) kilogram calories.

§4. Rotation of Molecules in Solids

Certain transitions occur between solid phases which, in contrast to the type just mentioned, may probably be profitably considered from the point of view developed in this paper. These are the transitions which are believed to be associated with the setting in of rotation of molecules which are not spherically symmetrical.[8] Such molecules, if not too unsymmetrical, may often be treated as though they were symmetrical if the temperature is high enough so that rotation has become established. However, at low temperatures we must expect a restriction on the rotation of the molecules, due to the presence of the other molecules, just as the translational motion is restricted.

The earlier sections of this paper suggest that we consider the extent of freedom of the rotation in relation to the molal volume at a given temperature. When the molal volume is small, the rotation is restricted, and we will have an extra contribution to $(\partial S/\partial V)_T$, because as the volume increases the rotational, as well as the translational degrees of freedom, are loosening up. Then, as we approach the point at which the rotation becomes practically completely free, there will be a certain range of volumes over which $(\partial S/\partial V)_T$ will decrease rapidly as the volume increases, till it reaches the value char-

[8] Pauling, Phys. Rev. **36**, 430 (1930).

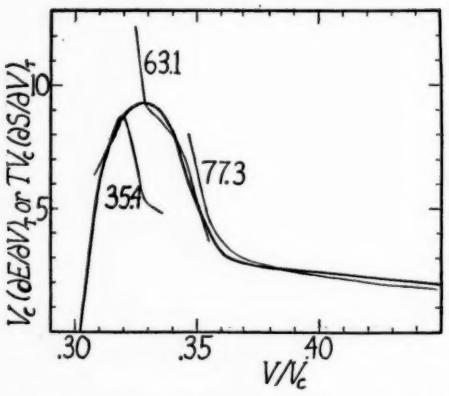

FIG. 4. Curves for N_2, small volumes. Heavy curve, $V_c(\partial E/\partial V)_T$; light curves, $TV_c(\partial S/\partial V)_T$ at temperatures indicated.

acteristic for translational degrees of freedom only. Such behavior could easily result in a transition point at which rotation sets in, or at least becomes considerably freer, as will be seen in §5. It is true that the same influences which change the $(\partial S/\partial V)_T$ curve may also cause some corresponding changes in the $(\partial E/\partial V)_T$ curve, but this should not alter the qualitative character of the phenomena.

Fowler[9] has recently developed a statistical theory of the rotation of molecules in which he considers the effect of an increase of temperature, any influence of the concomitant change of volume being neglected or relegated to a minor role. It is assumed that the probability of a given molecule rotating is much greater if its neighbors are already rotating, and he shows that under certain circumstances it is possible to get a sharp transition even though the volume does not change at all. However, we believe that it is probable that in the actually observed transitions the dependence of $(\partial S/\partial V)_T$ on volume plays an important part. Nevertheless, it seems altogether probable that there is a good deal of truth in Fowler's theory. Thus the greater ease of rotation for a molecule already in the neighborhood of rotating molecules would show up in a fairly great, though not completely sharp, increase of $(\partial S/\partial V)_T$ when the volume increases over a fairly narrow critical range just before the marked decrease of $(\partial S/\partial V)_T$ sets in. This would naturally affect the details of the transition. Furthermore, the exact volume at which $(\partial S/\partial V)_T$ decreases would depend upon the temperature, an effect which, in our first approximation, we neglect.

[9] Fowler, *Statistical Mechanics*, second edition (Macmillan, 1936) p. 810 ff.

§5. Application to Specific Cases

We shall now consider the application of the above ideas to a couple of specific cases, and attempt to construct $(\partial E/\partial V)_T$ and $(\partial S/\partial V)_T$ curves from the experimental data which are at hand. While it is not possible to get these curves exactly, a fairly good idea of their course may be obtained.

We start with N_2. In Fig. 3, we give the results for volumes down to the boiling point. It has been found convenient to divide all volumes by the critical volume V_c and present Fig. 3 in logarithmic form. This figure was constructed with the aid of the material in I[1(k)], and to avoid extensive repetition we shall, in explaining it, refer directly to I, using the symbols as there defined, and referring to the equations as Eq. I(1), for example. From Eq. (6) above, and from Eq. I(11), using the corrected value of γ obtained from I(23), we can obtain $(\partial S/\partial \log V)_T$, hence $T(\partial S/\partial \log V)_T$ and $(\partial E/\partial \log V)_T$ for the boiling point. This gives us one point on each of our curves. Next we construct a tentative curve for $(\partial E/\partial \log V)_T$, using Eq. (4). This enables us to construct the true $(\partial E/\partial \log V)_T$ curve with reasonable accuracy, inasmuch as we demand that the integral of $(\partial E/\partial \log V)_T$ taken between the volumes of the liquid and the vapor in equilibrium with it, be equal to γ times the integral under the curve obtained from Eq. (4).

Now, as stated, we already have $(\partial S/\partial \log V)_T$ at the boiling point. In addition, from I(15), we can, if we assume that γ is independent of V, and using again Eq. (6), obtain $(\partial^2 S/\partial (\ln V)^2)_T$, which gives us the slope of the curve for the point where V is equal to the volume of the liquid at the boiling point. We also know $(\partial S/\partial \log V)_T$ for large volumes where the vapor is a perfect gas, and furthermore we know the change of entropy on vaporization. These pretty well fix the curve. In the figure we also give the curve for $(\partial S/\partial \log V)_T$ which would be obtained by setting $(\partial S/\partial V)_T = R/(V-b)$, where b is an excluded volume similar to that introduced in

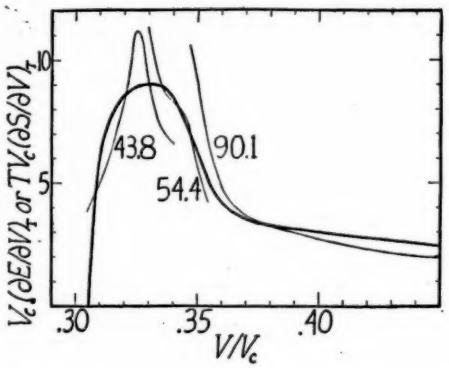

FIG. 5. Curves for O_2, small volumes. Heavy curve, $V_c(\partial E/\partial V)_T$; light curves $TV_c(\partial S/\partial V)_T$ at temperatures indicated.

the van der Waals equation. We have set $V_c=1.5b$. The van der Waals equation, if it held down to such low values of V, would give $V_c=3b$, while Loeb[10] suggests that the relation between V_c and the van der Waals constant is actually given approximately by $V_c=2b$, but this seems to lead to insuperable difficulties.[11] For the true value of $(\partial S/\partial V)_T$ must always be less than that given by the van der Waals equation, but it is impossible to fulfill this condition and at the same time have the curve fit the other data if V_c is set equal to $2b$. On the other hand, setting $V_c=1.5b$ gives very reasonable results, as will be seen from the figure.[12]

In Fig. 4, we give the $(\partial E/\partial V)_T$ curve for small values of V, and $T(\partial S/\partial V)_T$ for several temperatures, i.e., the boiling point, the melting point, and the transition point. These curves are very nearly fixed by the known molal volumes of liquid and solid N_2 at the melting point (31.6 and 29.6 cc, respectively),[13] the known heats of fusion and transition (172.3 and 54.7 calories per mole, respectively),[14] and the volume at absolute zero,[15] at which, at least approximately, $(\partial E/\partial V)_T=0$, and the volume at[16] 45°K. Further, the integral under the curve, taken between the respective volumes of the phases which are in equilibrium at any transition point, must equal the heat of transition. And, of course, the $T(\partial S/\partial V)_T$ curves must intersect the $(\partial E/\partial V)_T$ curve in just the right way at the transition point, as explained in §2.

In a similar manner curves for O_2 have been constructed. The figure for large volumes is very similar to Fig. 3, and is not reproduced. The result for small volumes is given in Fig. 5. In this figure the heats of fusion and transition check those of Giauque and Johnston[17] (106 and 178 calories per mole, respectively), the change in volume on fusion checks that found by Lisman and Keesom[18] (about 1.0 cc per mole) while the volumes below and above the transition just about coincide with the volumes derived from the densities of β and γ oxygen (1.395 and 1.30, respectively) found by Vegard.[19] The measured value of the liquid density seems to be in error,[20] but the value used in the diagram is consistent with the data on the solid and the volume change on fusion. We have made no attempt to account for the transition at 24°K, which has a small heat of transition. Taken as a whole, the picture which we have of the transitions in O_2 seems to be quite satisfactory, in spite of the fact that we have neglected entirely the possibility of special forces, connected with the magnetic moment of O_2, which might result in

[10] Loeb, *Kinetic Theory of Gas*, second edition (McGraw-Hill Book Co., 1934) p. 194.

[11] These difficulties are related to those mentioned in §2 of I (just after Eq. (15)), and I believe the matter is cleared up by the assumption that $V_c=1.5b$. It is still necessary, however, to suppose that $\phi(v)$ varies slightly from liquid to liquid.

[12] If a depends on the temperature, we have, from the thermodynamic relation $(\partial S/\partial V)_T=(\partial P/\partial T)_V$ and van der Waals equation, $(\partial S/\partial V)_T=R/(V-b)-(da/dT)/V^2$. If V is large this becomes, approximately, $R/V+(Rb-da/dT)/V^2$. Since da/dT will be expected to be negative (as a is closely related to a sort of association constant which gives the concentration of molecular pairs due to the van der Waals forces), b will be effectively increased, as far as the effect on $(\partial S/\partial V)_T$ is concerned.

[13] Landolt-Börnstein, *Tabellen*, 3. Ergänzungsband.

[14] Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).

[15] Density of N_2 is 1.026 at liquid hydrogen temperatures, according to *International Critical Tables*.

[16] Vegard, Zeits. f. Physik **79**, 471 (1932). The value of V/V_c for β N_2 at 45°K, from Vegard's x-ray determination of the density is found to be 0.317. Actually I have taken 0.3195 for V/V_c for β N_2 for the transition point at 35.4°K, but the difference is small, and on applying Eq. (8) my value gives a slightly smaller and, I believe, a somewhat more reasonable value for C_p-C_v. The average value of C_p-C_v obtained for the β range is approximately 3 calories per degree, which would give C_v an average value of about 7 calories per degree as compared to the value of C_v of 7.8 calories per degree for *liquid* air found by Eucken and Hauck, Zeits. f. physik. Chemie **134**, 161 (1928).

[17] Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).

[18] Lisman and Keesom, Physica **2**, 905 (1935).

[19] Vegard, Zeits. f. Physik **98**, 1 (1935).

[20] Keesom and Taconis, Physica **3**, 141 (1936).

the formation of a rather specific compound,[21] O_4.

Having constructed these curves, it is possible to apply Eq. (8), after integrating it over the range of existence of the liquid phase, and compare the experimental value of

$$\int_{T^f}^{T^b}(C_p-C_v)dT \quad \text{with} \quad \int_{V^f}^{V^b}(\partial E/\partial V)_T dV$$

taken from the curves. (In these equations the indices b and f refer to boiling and freezing points respectively.) We use the values of Giauque and his students for C_p a· d Eucken and Hauck's value for C_v for air. We find for

$$\int_{T^f}^{T^b}(C_p-C_v)dT$$

the values 82 and 178 calories for N_2 and O_2, respectively, while from the curves we get for

$$\int_{V^f}^{V^b}(\partial E/\partial V)_T dV$$

the values 107 and 127 calories for N_2 and O_2, respectively. The differences are probably not significant, as an error of a few percent in the densities could account for them. It is possible that the discrepancies indicate that some alteration of the curves would be desirable. However, it did not seem worthwhile to attempt to make them check in such detail, and it would probably not be possible to make the check absolute without assuming some error either in the densities at the boiling or freezing points, or in the coefficients of expansion at the boiling point.

It will be noted that the peculiar shape of the $(\partial S/\partial V)_T$ curve, which we use to account for the transition point in the solid, is just that to be expected for the setting in of molecular rotation,[22] as discussed in §4. We have not attempted to take into account any dependence on temperature of the value of V at which the sharp decrease in $(\partial S/\partial V)_T$ occurs. Thus the actual rate of the decrease at any given temperature can at best be roughly estimated from our curves. Nor have we attempted to take account of any possible effect on $(\partial E/\partial V)_T$.

It should perhaps be remarked that the transition temperatures of both oxygen and nitrogen, and the volumes at which these transitions occur, are sufficiently small so that quantization of the molecular motion is undoubtedly important. The bending over of the $(\partial S/\partial V)_T$ curve at small volumes, which accounts for the phenomenon of fusion, is itself undoubtedly connected with the setting in of quantization. One cannot, therefore, in general, assume that the $(\partial S/\partial V)_T$ curve will remain unaltered in shape when the temperature drops below the melting point, and insofar as this assumption is made it must be considered purely provisional.

§6. Some Quantitative Considerations Regarding the $(\partial S/\partial V)_T$ Curve for Liquids

As appears from I, the function $V(\partial S/\partial V)_T R^{-1} = (\partial V_e/\partial V)_T(V/V_e)$ plays a very important role in the theory of liquids. Since any information regarding the behavior of this function is of obvious interest in connection with the considerations of this paper, and since such information can be gleaned from the data already assembled in I, it seems worthwhile to close this paper with a few remarks on this subject. Eyring and Hirschfelder [1(j)] have suggested that it should be possible to set

$$(\partial V_e/\partial V)_T(V/V_e)=b(V/V_e)^{\frac{1}{3}}, \qquad (9)$$

where b does not vary with V, but, according to these authors, may depend on temperature. However, in the note[23] to I, we have given reasons for believing that $(\partial V_e/\partial V)_T(V/V_e)$ does not depend on temperature. If we make this assumption it is possible to test the correctness of setting the exponent in Eq. (9) equal to 1/3 by a

[21] See Lewis, J. Am. Chem. Soc. **46**, 2027 (1924), and Vegard, reference 19. Wahl, Proc. Roy. Soc. London **A88**, 61 (1913), reports that liquid O_2 can be supercooled down to the transition point, where the crystal modification, stable below that point, is formed almost instantaneously. This behavior is certainly not to be expected from Fig. 5, and if Fig. 5 comes anywhere near giving a correct picture of the equilibrium behavior of oxygen, it can only be explained on the assumption that internal equilibrium is not established rapidly in oxygen at low temperatures. It is to be remarked, however, that Giauque and Johnston found the melting point to be sharp, which is more nearly in accord with our expectations.

[22] It should be noted that the setting in of rotation will not necessarily be accomplished by a sharp change in phase. If the $(\partial E/\partial V)_T$ curve is at all points steeper than $T(\partial S/\partial V)_T$ there will be no definite change of phase, but there may well occur an anomaly in the specific heat. This would be particularly likely to occur if the transition takes place at a small volume. A number of cases of gradual transitions are known. For discussion and references see Pauling, reference 8, p. 441.

[23] Just following §3 of I.

method which we shall now develop. In general, of course, we can set, at least for a small range of volumes,

$$(\partial V_e/\partial V)_T(V/V_e)=b(V/V_e)^{1/n}, \quad (10)$$

where n is a constant. We then have

$$\frac{\partial \ln [(\partial V_e/\partial V)_T(V/V_e)]}{\partial \ln V}=n^{-1}\frac{\partial(\ln V-\ln V_e)}{\partial \ln V}$$
$$=n^{-1}(1-\partial \ln V_e/\partial \ln V). \quad (11)$$

The last term in Eq. (11) can be evaluated from I(11) where, of course, the corrected value of γ should be used. We have

$$\partial \ln V_e/\partial \ln V=(\Delta S/R-1)\gamma_{\text{corr.}}^{-1}=C'/\alpha RT, \quad (12)$$

where $C'=C_p$ (liq.) $-C_v$ (liq.). The last equation of Eq. (12) comes from I(23). On the other hand we have from Eq. I(15)

$$\frac{\partial \ln \phi}{\partial \ln V}=\frac{\partial \ln [(\partial V_e/\partial V)_T(V/V_e)]}{\partial \ln V}$$
$$=-(1/\alpha T+1/\gamma), \quad (13)$$

where now we must use the *uncorrected* value of γ, as explained in the note to I. This equation involves the assumption that γ is independent of V, but since γ never differs greatly from 1, this should be a good approximation. It also involves the assumption that $(\partial V_e/\partial V)_T(V/V_e)$ is independent of T, which has already been discussed, and which we believe to be correct. From Eqs. (11), (12) and (13), then, n can be determined, and the results for a number of the liquids considered in I are as follows: N_2, 1.59; CO, 1.82; A, 1.42; O_2, 1.49; HBr, 1.84; Cl_2, 2.05; $SiCl_4$, 3.10; Br_2, 2.23; CCl_4, 2.77. It should be noted that, though α may be in some error, the value of n is almost independent of α, since the calculation of γ also depends on α and since $C'/\alpha RT$ is considerably larger than 1. C' is obtained as explained in the note to I.

It is seen that n, for the most part, is considerably smaller than 3, and that the higher boiling substances have larger values of n. This result would appear to indicate that the assumption of Eyring and Hirschfelder can be only a rough approximation.

The New Absorption System of Cyanogen Gas in the Near Ultraviolet System I. Errata

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(J. Chem. Phys. **5**, 161 (1937)).

IN the following, we wish to correct a few typographical errors which appeared in our paper with the above title. On page 163, Table II, 33722 should read 33272. On page 165, ninth line below Table IV ν_2'/ν_2' should read ν_2'/ν_1'. :N⋮⋮C:C⋮⋮N: should read :N⋮⋮C:C⋮⋮N:

The Absorption Spectra and Dissociation Energies of Cyanic Acid and Some Isocyanates—A Correction

SHO-CHOW WOO AND TA-KONG LIU
Academia Sinica, Shanghai, China
(J. Chem. Phys. **3**, 544 (1935)).

On page 545, Table I, third column, 112.4 should read 114.6. On page 546, last paragraph, fifth line from bottom 52.4 should read 54.6; second line from bottom, C_2C_5 should read C_2H_5. The conclusion reached before remains unaltered by the above corrections.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Infrared Absorption Spectrum of Ketene

The infrared absorption spectrum of gaseous ketene has been measured from 740 to 3500 cm^{-1} with a rocksalt prism spectrometer with a Wadsworth-Littrow mounting. The ketene was especially pure[1] and we are indebted to Dr. W. E. Vaughan, Dr. Elgene A. Smith and Mr. M. A. Dolliver for the samples which we used. No absorption was found that could be ascribed to acetone, ethylene or methane, which would be the most probable impurities.

Intense bands have been found at 3058, 2160, 1935, 1400, 1110 and 890 cm^{-1}. Weaker bands have been found at 3165, 2915, 1350, 1325 and 1185(?) cm^{-1}. These absorption bands agree roughly with the Raman lines reported for the liquid by Kopper,[2] except that there is no infrared absorption corresponding to the Raman lines at 998 and 801 cm^{-1}, which, however, are considered doubtful by Kopper. Ketene has nine fundamental frequencies, all of which should be active in both Raman and infrared spectra.

We shall attempt to locate the fundamentals of the lower frequencies and make a complete analysis of the modes of vibration and force constants of the molecule. The description of the apparatus and the absorption curves will be published when the complete data are available.

HAROLD GERSHINOWITZ
E. BRIGHT WILSON, JR.

Department of Chemistry,
Harvard University,
Cambridge, Massachusetts,
May 10, 1937.

[1] The methods of preparation and purification will be described in paper No. 6 on "Heats of Organic Reactions" by Kistiakowsky *et al.*, which will appear in the J. Am. Chem. Soc. late in 1937.
[2] Kopper, Zeits. f. physik. Chemie **34B**, 396 (1936).